

**** Public Review Draft ****

Water Quality Guidance for the Great Lakes System
Draft Mercury Permitting Strategy

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MERCURY PERMITTING STRATEGY

Table of Contents

EXECUTIVE SUMMARY	i
INTRODUCTION	i
IMPLEMENTATION POLICY AND TOOLS	i
Total Maximum Daily Loads (TMDLs)	i
Intake Pollutant Procedures	ii
Water Quality-based Limits Below Level of Quantification and Pollutant Minimization Plans (PMPs)	iii
Site-specific Modifications to Criteria	iii
Point Source Variances	iv
DATA CONSIDERATIONS	iv
Historical Ambient and Effluent Data	iv
Detection Level Issues	iv
ANTIDegradation	v
SUMMARY	v
 I. PURPOSE	 1
 II. BACKGROUND	 1
 III. IMPLEMENTATION POLICY AND TOOLS	 3
A. ADJUSTMENTS TO STANDARDS	5
1. Site-specific Modifications to Mercury Criteria	5
a. Aquatic Life	6
b. Human Health and Wildlife	6
2. Point Source Variances for Mercury	6
B. DEVELOPING LIMITS BASED ON TOTAL MAXIMUM DAILY LOADS (TMDLs) AND ASSESSMENT AND REMEDIATION PLANS (ARPs)	7
1. General	7
2. Mixing Zones	9
C. DEVELOPING NPDES LIMITS IN THE ABSENCE OF A TMDL	10
1. Data to Assess Need for Mercury Controls	10
2. Reasonable Potential Determination	11
a. General	11
b. Determining Reasonable Potential With Effluent Monitoring Data	11
c. Determining Reasonable Potential Without Effluent Monitoring Data	12
d. Consideration of intake pollutants in determining reasonable potential	13
3. Establishing Permit Limits and Conditions	13

*** *Public Review Draft* ***

a.	General	13
b.	Limits Based on "No Net Addition"/Intake Credits	14
c.	Limits Below the Level of Quantification.	15
d.	Pollutant Minimization Plans	16
e.	New Analytical Methods	17
IV.	ANTIDEGRADATION	17
A.	INTRODUCTION	18
B.	OVERVIEW OF GUIDANCE ANTIDEGRADATION PROVISIONS	18
1.	Protection of Existing Uses	18
2.	Protection of High Quality Waters	18
3.	Outstanding National Resource Waters	19
V.	SUMMARY	19

APPENDICES

A.	Summary of Other EPA, State, and Tribal Mercury Initiatives and Programs [Forthcoming]
B.	Implementation Flow Chart
C.	Developing Site-Specific Modifications To Criteria for Mercury
D.	Quality Assurance/Quality Control (QA/QC) Recommendations
E.	List of Resources/Contacts [Forthcoming]

MERCURY PERMITTING STRATEGY

EXECUTIVE SUMMARY

INTRODUCTION

Mercury use in the United States has decreased by approximately 72% from 1983 to 1994. Industrial consumption of mercury in the United States went from 1,503 metric tons in 1988 to 720 metric tons in 1990. The rate of decline, however, has slowed since 1990. For the years 1991, 1992 and 1993, industrial consumption of mercury amounted to 554, 621 and 558 metric tons, respectively. During this same time period (1990-1993), secondary mercury production (e.g., from recovery operations) increased from 15 percent of total industrial consumption in 1990 to 63 percent in 1993. The three facilities which produce the bulk of secondary mercury in the United States are located in the Great Lakes States of Illinois, New York and Pennsylvania. Currently, the remaining significant contributors of mercury releases to the waterbodies in the Great Lakes Basin are nonpoint sources, especially atmospheric deposition.

The purpose of the Mercury Permitting Strategy ("Strategy") is to identify how the Great Lakes Water Quality Guidance ("Guidance"), promulgated on March 23, 1995, provides for implementation of mercury water quality standards through NPDES permits for point sources, focusing on the flexibility States or Tribes have for adjusting point source controls to account for non-point sources of mercury. The Strategy also addresses several permit implementation issues related to the particular nature of mercury. Finally, the Strategy describes how antidegradation provisions of the Guidance related to BCCs may affect point source controls. The goal of the strategy is to advance the goal of virtual elimination of mercury as called for in the Great Lakes Water Quality Agreement and the Binational Virtual Elimination Strategy while providing options for cost-effective implementation that consider the sources of mercury. In pursuing these goals, EPA strongly encourages mercury reduction strategies based on pollution prevention approaches.

IMPLEMENTATION POLICY AND TOOLS

The Guidance contains a number of implementation tools that allow permitting authorities to consider the multiple sources of mercury when determining appropriate waste load allocations for point source dischargers. Other procedures specify how mercury will be regulated through NPDES permits. The key features of significant provisions are described below:

Total Maximum Daily Loads (TMDLs): EPA strongly encourages States initially to consider development of TMDLs or one of the alternative assessment and remediation plans (ARPs), described in Appendix F, Procedure 3 of the Guidance, for mercury in waters that exceed the applicable criteria before establishing controls for point source dischargers. The primary advantage of TMDLs or alternative assessment and remediation plans is that they can account for the multi-media and multi-source characteristics

common to mercury contamination and facilitate implementation of remediation measures to ensure attainment of water quality standards. Significantly, under some circumstances, through use of a phased approach to TMDL development, a State or Tribe can account for future reductions in nonpoint source loadings in calculating current wasteload allocations for point sources. In this way, States or Tribes can avoid requiring point sources to remove pollutants contributed by other sources when there are reasonable assurances that reductions from other sources will be forthcoming and water quality standards achieved.

The Guidance prohibits mixing zones for new Great Lakes discharges (as of March 23, 1997). The Guidance's prohibition on mixing zones for BCCs after March 23, 2007 for existing discharges will limit the flexibility of States and Tribes to adopt less stringent effluent limits for existing mercury discharges predicated on anticipated reductions from nonpoint sources unless the discharger qualifies for one of the two exceptions to the prohibition. Regardless of the implications for particular dischargers, EPA continues to believe that TMDLs are a powerful tool for understanding contributions from other sources and what reductions might be achieved by those sources because they provide information for developing comprehensive strategies to achieve water quality standards. Moreover, a multi-source TMDL analysis can provide necessary information to assess whether an exception to the mixing zone ban based on technical or economic infeasibility for a particular discharger is warranted.

Intake Pollutant Procedures: EPA expects that States and Tribes will not be able to prepare TMDLs immediately for all waterbodies that exceed standards and have point sources contributors of mercury. In the interim, EPA recommends that an intake pollutant analysis be considered anytime mercury has been detected in the effluent (or a tentative reasonable potential finding has been made on the basis of other information), but there are no known sources of additional contributions of mercury at the facility. Procedure 5 D. in Appendix F provides for a finding of no reasonable potential when the only source of a pollutant of concern in the discharge is the intake water from the same body of water as the discharge and other conditions are met related to the water quality impacts of the discharge. Even where there are known additional contributions of mercury to the wastestream at the facility, but other conditions for intake pollutant relief are met, dischargers may still be eligible for relief in the form of "no net addition" limits under Procedure 5.E if the levels of the pollutant in the background water of the discharge exceed the most stringent criteria. This approach allows the discharger to discharge the amount of mercury in its intake waters but not an additional amount. Thus it relieves the discharger from having to remove mercury from the background water originating from other sources, but requires the discharger to eliminate any incremental amount of mercury in the discharge that originates at the facility.

To encourage States to develop TMDLs or ARPs, the Guidance limits the availability of

special permitting procedures for considering intake pollutants in setting water quality-based effluent limits (WQBELs) ("no net addition" limits) to the first ten years after States are to implement the Guidance. The Council of Great Lakes Governors has indicated its members' intent to develop TMDLs or ARPs within this time frame. EPA and the States recognize that progress in developing TMDLs should be reevaluated at "mid-point" to determine if the phase-out of no net addition limits remains appropriate.

Water Quality-based Limits Below Level of Quantification and Pollutant

Minimization Plans (PMPs): Procedure 8 of Appendix F requires a permit to contain a WQBEL exactly as calculated even where the limit is below the level of quantification. The Guidance defers to State and Tribal procedures for averaging values below the level of quantification for purposes of compliance assessment. Mercury limits are likely to be below the level of quantification using the currently approved EPA method. In this situation, the permittee must undertake a Pollutant Minimization Plan (PMP) to identify possible sources of mercury to its system, assess control strategies and implement cost-effective measures with the end goal of ensuring compliance with the WQBEL. (Also see the related discussion on detection levels issues below.)

EPA anticipates that the PMP will serve to emphasize the opportunities afforded by source reduction up front, rather than by traditional reliance on end-of-pipe treatment. While Procedure 8 does not prohibit treatment as an alternative for reducing mercury levels in the effluent, EPA notes that a pollution prevention approach for reducing mercury may well have the added advantage of reducing mercury releases to other media. Because mercury releases from other media are known to impact water quality, any reduction in mercury releases has the potential to benefit point sources by reducing mercury levels in either or both a facility's source and receiving water.

Pollution prevention also plays a significant role in other implementation procedures under the Guidance. The first step of an antidegradation analysis for BCCs is to identify any and all cost-effective pollution prevention alternatives that might eliminate or reduce the proposed significant lowering of water quality. Similarly, a State or Tribe can grant an

exception to the mixing zone prohibition only if feasible alternative control strategies, including pollution prevention, do not exist. Clearly, EPA regards pollution prevention as an important and effective element in the control of mercury.

Site-specific Modifications to Criteria: Procedure 1 of Appendix F provides for site-specific modifications to criteria. Under this procedure, site-specific factors that differ from those in establishing the criteria adopted in the Guidance can justify more or less stringent criteria for human health, wildlife, and aquatic life. While less stringent criteria are possible for all three mercury criteria, EPA considers the bioaccumulation factor the most likely component in the derivation of wildlife and human health mercury criteria that could be changed on a site-specific basis; lower fish consumption rates in the affected populations may also provide a basis for less stringent human health criteria. The Strategy includes a technical appendix that provides guidance on developing site-specific modifications in these situations. Site-specific criteria modifications do not address directly the question of nonpoint source impacts on water quality, although they do provide for adjustments to criteria which may obviate the need for additional point source controls on mercury.

Point Source Variances: Procedure 2 of Appendix F allows States and Tribes to provide existing Great Lakes dischargers relief from a water quality standard in the form of a temporary variance to the standard under certain circumstances. Variances for mercury might be useful in situations where other implementation tools are not available or feasible, i.e., where the State has not prepared a TMDL or ARP and intake pollutant procedures are not available (for example, where the intake pollutants are from a different body of water than a discharge), and site-specific criteria modifications cannot be justified or documented. Traditionally, variances are chemical-specific and facility-specific; however, for situations where a number of dischargers are located in the same watershed, and the circumstances for granting a variance are the same, EPA encourages States or Tribes to consider administering a multiple-discharger variance for a group of dischargers collectively, at the same time.

DATA CONSIDERATIONS

Historical Ambient and Effluent Data: An important consideration in implementing water quality criteria for mercury is data quality, particularly with respect to historical data where either the permittee or permitting authority suspects sample contamination problems. While existing data generated under the existing Part 136 method is valid, new data can be generated in ways to minimize or eliminate sample contamination concerns. EPA supports use of additional Quality Assurance/Quality Control (QA/QC) measures when obtaining new data to make necessary regulatory decisions, such as the water quality status of a particular water body or the need for WQBELs. Certainly, absence of data or speculative concerns about sample contamination are not acceptable reasons for failing to

implement necessary regulatory controls. On the other hand, data supplemented by QA/QC samples and/or obtained using "clean techniques" may demonstrate that a previously identified concern with mercury in the ambient water or a particular effluent was due to sample contamination rather than an actual problem. The Strategy contains recommendations and a technical appendix on Quality Assurance/Quality Control measures for generating or evaluating mercury data.

Detection Level Issues: EPA's current methods for analyzing mercury in water and wastewater samples in 40 CFR Part 136 have a detection level of 0.2 µg/L as compared to the Great Lakes mercury criterion for human health of 1.8 ng/L (total); the acute aquatic criteria of 1.44 µg/L (dissolved); the chronic aquatic criteria of 0.77 µg/L (dissolved); and wildlife criteria of 1.3 ng/L (total). The Strategy reaffirms the use of the existing Part 136 method for analyzing mercury samples (245.1), but also expresses EPA's recommendation that States or Tribes consider data generated by the newer Method 1631 as valid for regulatory purposes discussed in the Strategy, such as reasonable potential analysis or demonstrations of compliance with a WQBEL below the level of quantification. The Strategy addresses incorporating new, more sensitive analytical methods for compliance assessment purposes when they are available. At the same time, the Strategy recognizes that States or Tribes may want to consider compliance schedules for phasing-in the use of a new analytical methods to assess compliance for permittees with an existing WQBEL.

ANTIDEGRADATION

The antidegradation provisions of the Guidance are intended to protect the Great Lakes System from new and increased loadings of BCCs. The Guidance supplements existing antidegradation regulations by providing more detailed information about how to implement the antidegradation requirements for BCCs. Antidegradation requirements must be met independently of what might be allowed through the implementation procedures identified above. The need for an antidegradation review is triggered by new or increased loadings, rather than by point source controls. The Strategy summarizes the antidegradation provisions and explains the role of the NPDES program in the implementation of those provisions.

SUMMARY

The Guidance contains a number of mechanisms for adjusting point sources controls that directly or indirectly authorize States or Tribes to account for nonpoint source contributions to mercury impairment of the Great Lakes system. In the short-term, use of the mechanisms can help to minimize the need of requiring reductions from point sources in some cases where multiple sources are involved. Ultimately, however, what will be needed is comprehensive reduction of mercury due to human activity so as to maintain and achieve water quality standards.

MERCURY PERMITTING STRATEGY

I. PURPOSE

Great Lakes Regions, States, and Tribes have a number of efforts underway to identify and implement approaches for reducing the amount of mercury in the Great Lakes System. This strategy is not intended to duplicate or replace these efforts. Appendix A describes these efforts, as well as activities at the federal level related to reduction of mercury in the environment. Rather, the purpose of this Strategy is to identify how the Guidance provides for implementation of mercury water quality standards through NPDES permits for point sources, focusing on the flexibility States or Tribes have for adjusting point source controls to account for nonpoint sources of mercury, and site- and discharger-specific factors.

The Strategy also addresses a number of permit implementation issues related to the particular nature of mercury, including data considerations associated with data quality and limits below the level of quantification. The goal of the strategy is to advance the goal of virtual elimination of mercury as called for in the Great Lakes Water Quality Agreement and the Binational Virtual Elimination Strategy while providing options for cost-effective implementation that consider the sources of mercury. In pursuing these goals, EPA strongly encourages mercury reduction strategies based on pollution prevention approaches.

II. BACKGROUND

A key to achieving the Clean Water Act's (CWA) goal of restoring and maintaining the chemical, physical and biological integrity of the nation's waters is prohibiting the discharge of pollutants unless authorized through the National Pollutant Discharge Elimination System (NPDES) program. See CWA Section 301(a). Permits issued pursuant to this program provide for limitations on discharges that reflect the pollution reduction achievable by specified levels of technological controls, and any more stringent limitations necessary to protect the quality of the receiving waters.

Water quality standards represent the water quality goals established for waters of the U.S.. They consist of : 1) designated uses for specific waterbodies; 2) criteria specifying maximum concentrations of pollutants that can be present in the waterbodies while still ensuring achievement and maintenance of the designated uses; and 3) an antidegradation policy to protect existing uses and high quality waters. The most important component of a water quality standard for purposes of establishing water quality-based effluent limitations is water quality criteria. Water quality-based effluent limits (WQBELs) are included in NPDES permits if water quality standards will not be met even after implementation of technology-based controls on point sources and if the permitting authority determines that the permittee's discharge causes or has the reasonable potential to cause or contribute to an exceedance of the water quality standard.

On March 23, 1995, EPA published in the *Federal Register* Final Water Quality Guidance

for the Great Lakes System (Guidance). The Guidance consists of water quality criteria for 29 pollutants to provide minimum levels of protection for aquatic life, human health and wildlife of the Great Lakes; detailed methodologies to develop criteria for additional pollutants; implementation procedures to develop more consistent enforceable WQBELs in discharge permits, as well as total maximum daily loads of pollutants that can be allowed to reach the Lakes and their tributaries from all sources; and antidegradation policies and procedures. The Guidance will help establish consistent, enforceable, long-term protection from all types of pollutants, but will place short-term emphasis of the types of long-lasting pollutants, such as mercury, that accumulate in the food web and pose a threat to the Great Lakes System.

During the development of the Guidance, EPA addressed the problem posed in controlling the discharge of mercury in particular. Mercury can enter water bodies through direct discharge, nonpoint runoff, or from atmospheric deposition, which is the most significant source. Mercury as an air pollutant is released from a variety of natural and anthropogenic areas, and from sources such as combustion and manufacturing processes. The mercury that is deposited in the Great Lakes System originates from the manufacturing and processing of this chemical, as well as from ancillary or other uses. The atmosphere, however, is the dominant pathway by which mercury reaches the Great Lakes. An emissions inventory conducted for EPA's forthcoming Clean Air Act Mercury Study estimates that medical and municipal waste incinerators, coal-fired electric utilities, mercury cell chlor-alkali plants, primary copper and primary lead smelters, cement manufacturers, and secondary mercury production facilities are the industrial sectors that emit the largest quantities of mercury to the atmosphere.

The Guidance also identified a class of highly bioaccumulative chemicals of concern (BCCs) which tend to persist throughout the Great Lakes ecosystem, have a propensity to bioaccumulate in the food chain, and have been associated with serious and system-wide impacts. The BCCs were defined as chemicals which bioaccumulate in aquatic organisms by a human health bioaccumulation factor (BAF) greater than 1000. The BAFs are derived based on the relationship between fish tissue concentrations and water column concentrations of pollutants. The BAF for mercury was derived based on the percentage of methyl mercury and amount of trophic uptake as explained in Appendix D of the July 1994 Technical Support Document for BAFs (EPA-822-R-94-002). The baseline BAF for mercury for both wildlife and human health criteria and values for trophic level 3 (small fish) are 27,900, and 140,000 for trophic level 4 (top predator fish). Twenty-two chemicals, including mercury, were designated as BCCs in the final Guidance. Special provisions applicable to BCCs were included in the Guidance and are designed to ensure that future problems associated with these chemicals are minimized, overall loadings of these chemicals to the Great Lakes are reduced, under-regulation of these chemicals because of lack of data does not occur, and water quality criteria that will protect wildlife that feed on aquatic prey are developed.

The Guidance included a human health mercury criterion of 1.8 ng/L for both drinking water and nondrinking water sources. This criterion was based on a human health RfD of 0.06

ug/kg/day. Shortly before promulgation of the Guidance, EPA revised its estimate of the human health RfD for mercury to 0.1 ug/kg/day. Assuming no changes to any other component of the criterion, this revised RfD would result in a revised human health mercury criterion of 3.1 ng/L.

The RfD of 0.06 ug/kg/day used in the Guidance was based on a lowest observed effects level (LOAEL) of 3 ug/kg/day divided by an uncertainty factor of 50. The uncertainty factor of 50 was composed of a 10-fold factor to adjust the LOAEL to a no observed adverse effect level (NOAEL) and an additional 5-fold factor to ensure the criterion will provide protection from the potential fetal effects of mercury exposure via maternal ingestion of mercury contaminated fish. The 5-fold uncertainty factor was justified to protect central nervous systems development during the fetal life stages.

The revised RfD of 0.1 ug/kg/day is based on a benchmark dose of 1.0 ug/kg/day and an uncertainty factor of 10. The uncertainty factor of 10 is composed of a 3-fold factor for variability in the human population and another 3-fold factor for lack of a two-generation reproductive study.

In March 1996, EPA issued guidance explaining that it plans to consider State and Tribal standards based on revisions to EPA's RfD to be "as protective as" the criteria promulgated in the 1995 Guidance. "Questions and Answers on Implementing the Great Lakes Guidance," March 29, 1996, Question # 3. Therefore, State and Tribal standards based on either the old or the revised RfD will be eligible for approval. More recently, EPA announced that it intends to propose to revise the current Great Lakes human health criterion for mercury to reflect the revised RfD. If EPA promulgates such a revision, the States and Tribes will continue to have the option of basing their mercury standards on the earlier RfD, since they have authority to adopt standards that are more stringent than EPA's.

III. IMPLEMENTATION POLICY AND TOOLS

Although nonpoint sources are widely recognized as significant sources of mercury releases in some areas, control of mercury from point source discharges will continue to be important to ensure that, in general, point source contributions of mercury do not increase and, where appropriate, additional controls are implemented to reduce mercury discharges to ensure attainment of water quality standards. EPA supports the use of intake credits and TMDLs prior to 2007 to authorize point source discharges at background levels in many situations, but notes that after March 23, 2007, Guidance provisions are less flexible and will require many dischargers to achieve limits set equal to criteria.

The Guidance contains a number of implementation tools that allow the permitting authority to consider the multiple sources of mercury when determining appropriate waste load allocations for point source dischargers. (See the Supplementary Information Document or SID for a full discussion of all Guidance provisions discussed below.) As an initial matter, EPA

strongly encourages States and Tribes to consider development of Total Maximum Daily Loads (TMDLs) or an alternative assessment and remediation plan (ARP) described in Appendix F, Procedure 3 of the Guidance, for mercury in waters that exceed the applicable criteria, before establishing controls for point source dischargers. The advantage of these approaches is that they can account for the multi-media and multi-source characteristics common to mercury contamination and facilitate the implementation of comprehensive remediation measures to ensure attainment of water quality standards. While the Guidance provides tools for adopting less stringent effluent limits for mercury predicated on anticipated reductions from nonpoint sources, ultimately resolving the underlying non-attainment problem will provide the greatest assurance that point sources alone are not held responsible for addressing or mitigating multi-source contamination problems.

The Guidance and this Strategy also address development of point sources controls in the absence of TMDLs and discusses available mechanisms within the standards and permits programs for adjusting point sources controls on mercury. This Strategy also covers various mercury data issues such as quality, interpretation and detection level. The remainder of this section describes the mechanisms available for adjusting point source controls to account for other sources of mercury and how mercury should be evaluated in developing permits for individual dischargers.

The following section is organized along the "standards-to-permit" process, and reflects EPA's preference for TMDLs as the basis for establishing point source wasteload allocations when there are multiple sources contributing to a standards exceedance. However, as a practical matter, TMDLs will not be available for developing WLAs in many cases. Further, deciding if and how to establish mercury controls for a particular discharger requires consideration of several possible implementation approaches that vary from the relatively simple to the complex. Appendix B is a flow chart that describes a decision-making sequence of actions a permitting authority could use to consider the simplest approaches (e.g., is there a real water quality problem or a sample contamination problem) before proceeding to more complex approaches (e.g., developing a site-specific criterion).

A discussion of the antidegradation provisions of the Guidance and implications for point source controls closes this section.

A. ADJUSTMENTS TO STANDARDS

NPDES permits contain requirements to implement water quality standards when technology-based controls are insufficient to attain or maintain water quality standards in the receiving water. As discussed above, EPA has agreed to publish a new human health criterion for mercury based on the Agency's new RfD. In the interim, EPA has also advised States and Tribes that it would approve a mercury human health criterion based on either the old or new RfD. In most cases, however, the wildlife criterion will govern as the most stringent of the criteria. An

exception would be where a site-specific modification to the wildlife criterion is less stringent than the human health criterion.

Appendix F of the Guidance contains two implementation procedures related to the adjustment of water quality standards: Procedure 1, which addresses site-specific modifications to water quality criteria; and Procedure 2, which addresses temporary variances to water quality standards. An adjustment to the water quality criteria may be considered at the outset, but as a practical matter, it is often not considered until after an evaluation of the need for water quality-based effluent limits ("WQBELs") during the permit development process. Water quality variances usually are tied to the discharger's ability to meet a water quality-based limit and therefore also are typically considered after an evaluation of controls necessary to implement water quality standards. These Guidance mechanisms for adjusting standards do not directly address the relationship between point and nonpoint source contributions of mercury to a particular body of water in setting limits for point source discharges. However, a direct adjustment to the standard could result in eliminating the need for WQBELs or, where WQBELs are needed, result in less stringent limits. Each procedure, and its application to mercury discharges, are described below.

1. Site-specific Modifications to Mercury Criteria

Procedure 1 of Appendix F of the Guidance allows for more or less stringent modification of these criteria on a site-specific basis to reflect local environmental conditions. More stringent aquatic life, wildlife, and human health criteria could be derived on a site-specific basis to provide an additional level of protection, pursuant to authority reserved to the States and Tribes under CWA section 510. Less stringent site-specific modifications must be protective of designated uses and aquatic life, wildlife, or human health and submitted to EPA for approval. In addition, any site-specific modifications that result in less stringent criteria must be based on a sound scientific rationale and must be unlikely to jeopardize the continued existence of endangered or threatened species listed or proposed under section 4 of the Endangered Species Act (ESA) or result in the destruction or adverse modification of such species critical habitat. As with any site-specific modification criteria, implementation must also ensure protection of downstream uses.

a. **Aquatic Life:** Appendix F, Procedure 1.A.1. describes when more or less stringent criteria for aquatic life (acute and chronic) can be considered. Briefly, the site factors which may support a less stringent criterion include: (1) local water quality characteristics that alter the biological availability or toxicity of a pollutant; (2) sensitivity of the aquatic organisms that occur at the site that differ from the species tested in developing the criteria; or (3) local physical and hydrological conditions. Chapter 3 of the U.S. EPA Water Quality Standards Handbook, Second Edition, Revised (USEPA, 1994) provides additional guidance on developing site-specific criteria for acute or chronic aquatic life criteria.

b. Human Health and Wildlife: The Guidance provides for more or less stringent criteria for either human health and wildlife based on a site-specific bioaccumulation factor (BAF) and specifies requirements when this adjustment is undertaken. It also provides for adjustment to human health criteria based on different fish consumption rates than those used in developing the criteria. The Guidance does not preclude consideration of other site-specific factors in developing less stringent criteria (e.g., wildlife population), although EPA expects that adequate justification would be very difficult to develop. Appendix C of this Strategy provides additional technical guidance on developing site-specific modifications for human health and wildlife criteria, including a brief overview of mercury speciation and cycling in surface waters, a discussion of the components of the mercury criteria derivation which can be modified site-specifically, and the different approaches available for modifying the bioaccumulation factor (BAF), which is the component of the mercury criteria most likely to be modified on a site-specific basis for human health and wildlife.

2. Point Source Variances for Mercury

Procedure 2 of Appendix F to Part 132 allows States and Tribes to provide existing Great Lakes dischargers relief from a water quality standards in the form of a variance to the standards. The variance, in effect, provides a substitute standard for the point source; water quality-based limits would be based on that substitute standard. New and recommencing dischargers are not eligible for variances under Part 132. Part 132 identifies the terms and conditions which must be met if a State or Tribe wants to grant a variance. Traditionally, variances are chemical-specific and facility-specific. For situations where a number of dischargers are located in the same watershed, and the circumstances for granting a variance are the same, a State or Tribe may wish to process a multiple-source variance for a group of dischargers collectively, at one time. The State or Tribe would need to make a showing that all of the individual facilities in a group meet the terms and conditions described in procedure 2 of appendix F to Part 132. After the multiple source variance is approved for the initial group of facilities, additional facilities could be included in the multiple source variance, provided they met the terms and conditions of procedure 2. As with individual variances, a multiple source variance would be subject to review and approval by U.S. EPA; however, individual agreements between the States or Tribes and their respective U.S. EPA Regional offices could be developed to streamline such review and approval.

In addition to the specific requirements of procedure 2, a State or Tribe must make a showing that each of the individual facilities in a specific group meets the criteria for granting a variance, and:

1. Identify the facilities proposed for coverage under the variance;
2. Identify the geographic area of the watershed impacted by the variance;
3. Evaluate the geographic area for the existence of any endangered or threatened species listed under Section 4 of the Endangered Species Act; and

4. Recertify the eligibility of individual facilities at a minimum of every 5 years, or at the time of permit reissuance, whichever is less.

As with any variance granted under Procedure 2, a discharger subject to a multi-source variance must continue to implement all applicable technology-based treatment and pretreatment requirements of CWA sections 301, 302, 304, 306, 307, 401 and 402 and WQBELs not affected by the variance.

B. DEVELOPING LIMITS BASED ON TOTAL MAXIMUM DAILY LOADS (TMDLs) AND ASSESSMENT AND REMEDIATION PLANS (ARPs)

1. General.

TMDLs quantify the maximum allowable loading of a pollutant (plus a margin of safety) to a water body, and allocate this loading capacity to contributing point and nonpoint sources (including natural background, in-place contaminants, direct wet and dry deposition, groundwater inflow, and overland runoff) such that applicable water quality standards will be attained. Procedure 3 of Appendix F of the Guidance establishes additional specific requirements for TMDLs. These requirements in Procedures 3 are in addition to the requirements in the national TMDL regulations and recommendations in national guidance, both of which continue to apply to TMDLs developed pursuant to Procedure 3. Criteria for EPA approval of TMDLs continue to be governed by 40 CFR 130.7. Procedure 3 of the Guidance establishes minimum requirements for TMDL development, while maintaining considerable flexibility for States and Tribes in determining the area covered by a particular TMDL, how to achieve cost-effective allocation of available loadings, and what priority to give TMDL development for a particular waterbody. Procedure 3 also recognizes alternative Assessment and Remediation Plans (ARPs) efforts such as Lakewide Management Plans and Remediation Assessment Plans that may not have undergone the necessary steps for TMDL approval under Section 303(d) of the CWA and implementing regulations, but that meet the requirements in Procedure 3 and thus achieve the same water quality protection as TMDLs for purposes of Appendix F of the Guidance. (Subsequent references to TMDLs include eligible ARPs.) When an approved TMDL is in place covering a particular discharger, a separate reasonable potential determination under Procedure 5 for that discharger is not necessary before imposing a WQBEL. (Note, however, that a State or Tribe could use the reasonable potential procedure to determine that a WQBEL is not necessary, if the anticipated effluent quality is not expected to exceed the WLA in the TMDL.) The NPDES permit limit would then be based on the wasteload allocation for the discharge contained in the TMDL. States and Tribes should use existing procedures for translating WLAs into water-quality based effluent limits. (Procedure 5.F.2.b.)

A TMDL is EPA's preferred approach for addressing non-attainment of water quality standards for water impacted by multiple sources because it provides for a comprehensive assessment of contributing sources and facilitates implementation of plans to attain standards.

TMDLs are particularly well-suited for developing water quality-based controls for mercury dischargers in the Great Lakes System, because they can directly account for nonpoint source contributions of mercury in calculating point source limits. When data, models, and predictive tools are not yet fully developed to address complex water quality situations characterized by persistent, ubiquitous pollutants and water quality impacts resulting from nonpoint sources of pollution, as in the case of mercury, EPA encourages the use of a phased approach to TMDL development. A phased approach to TMDLs allows States and Tribes to consider anticipated decreases in pollutant loadings from nonpoint sources if such decreased loadings are technically feasible and if the State or Tribe has reasonable assurances that the reductions will occur within a reasonable time period. The additional capacity created by these anticipated reductions in nonpoint source loadings may then be allocated to point source loadings as appropriate (provided of course that the adjustment is consistent with the State's or Tribe's antidegradation policy). The Guidance does not specify when anticipated reductions and attainment of water quality standards must occur. Instead this is a case-by-case determination that would consider a number of factors including, but not limited to, receiving water characteristics, persistence, behavior and ubiquity of the pollutant, type of remediation activities necessary, available regulatory and non-regulatory controls and individual State or Tribal requirements for the implementation of water quality standards.

The Clean Water Act gives States and Tribes the flexibility to allocate pollutant load reductions among sources as they see fit, provided that the TMDL is designed to achieve attainment of applicable water quality standards and incorporates a margin of safety. Thus, the Guidance recognizes that specific wasteload and load allocations may be analyzed in light of the potential costs to individual sources of the pollutant in question as well as to the community at large. The TMDL provisions in the Guidance and the existing national program requirements for TMDLs support the use of cost-effectiveness analysis as one factor to consider in recommending potential allocations. In the Supplementary Information Document, EPA generally encouraged States and Tribes to consider pollutant trading opportunities when developing TMDLs. Certainly, a major policy goal for a TMDL is to implement the most cost-effective approach for achieving necessary reductions considering the various sources and available reduction opportunities. However, subsequently, in the Draft Framework for Watershed-Based Trading [Office of Water, EPA 800-R-96-001, May 1996], EPA noted that trading approaches for persistent and bioaccumulative toxic pollutants might be inadvisable because it could lead to localized violations of water quality standards.

2. **Mixing Zones:** Under the Guidance, mercury is a bioaccumulative pollutant of concern (BCC). Procedure 3 of Appendix F of the Guidance provides for the immediate (i.e., as of March 23, 1997) prohibition of mixing zones for BCCs for new or expanded discharges and the phase-out of mixing zones for existing discharges in 10 years following required State and Tribal implementation of the Guidance. The ban on mixing zones for BCCs limits the flexibility States and Tribes would otherwise have to adjust point sources controls based

on nonpoint source contributions through the phased approach to TMDL development. However, the ban in 2007 pertaining to existing discharges is not absolute.

The Guidance authorizes mixing zones after March 23, 2007 for existing discharges of BCCs in two circumstances: first, where the absence of a mixing zone would preclude water conservation measures that would lead to overall BCC load reductions; and second, where the discharger is in compliance with its existing NPDES permit conditions and has reduced its loadings of the BCC for which the mixing zone is sought to the maximum extent possible. See Procedure 3.C.5 & 6. In making the determination whether the BCC loadings have been reduced to the maximum extent possible, the permitting authority should consider, among other things, (1) the availability and feasibility of additional controls and pollution prevention measures, and (2) whether the discharger will experience unreasonable economic effects if the mixing zone is eliminated. See Procedure 3.C.6.b. Assuming that the existing discharge qualifies for a BCC mixing zone, the Guidance then specifies limitations regarding the size and duration of the mixing zone. Procedure 3.C.6.c. For example, the Guidance provides that the mixing zone must be consistent with any appropriate TMDL. Thus, if the discharger qualifies for the BCC mixing zone exception in accordance with Procedure 3.C.6.a & b, and the appropriate TMDL authorizes a sizable mixing zone for the existing BCC discharge, then under the Guidance the mixing zone may be as large as the TMDL allows, subject to endangered species and other considerations set forth in Procedure 3.C.c.

The final Guidance does not specify when or in what priority States and Tribes must develop TMDLs. Although the Great Lakes States, through the Council of Great Lakes Governors, have committed in principle to developing all necessary TMDLs by March 2007, it is important to recognize that even under the phased approach, anticipated nonpoint source controls may not be sufficient to attain water quality standards for mercury. In these situations, a TMDL could not be used to relax limitations applicable to point sources. Nevertheless, EPA believes that it remains critically important to pursue all feasible reductions in mercury loadings even in these circumstances. Ultimately, reduction in background concentrations of mercury will be the only reliable way to ensure that point sources will not be required to remove background levels of mercury originating with other sources.

C. DEVELOPING NPDES LIMITS IN THE ABSENCE OF A TMDL

1. Data to Assess Need for Mercury Controls.

The Guidance does not specify application data requirements for evaluating the need for water quality-based effluent limits. Instead, the NPDES regulations at 40 CFR 122.21 (and State or Tribal equivalents) establish minimum requirements. States and Tribes may need to supplement this data, prior to permit issuance or through permit conditions, to ensure adequate data for water quality-based control decisions. When characterizing an effluent to determine the need for a water quality-based effluent limit, permit writers should use available effluent

monitoring data as well as other information pertaining to the discharge as the basis for a decision. The reasonable potential discussion below (section III.C.2) further addresses data use and interpretation.

A major concern with mercury data has been data quality. Mercury analyses must be adequately documented and properly conducted to demonstrate that the data are acceptable and not contaminated. Minimally, States and Tribes should require applicants to provide the information necessary for permit writers to confirm that all of the following requirements pertaining to the generation of mercury data have been satisfied. Briefly, permittees must analyze 24-hour composites for mercury (40 CFR §§ 122.21(g)(7)) by a test method specified in Table IB of §136.3(a), using the preservation procedures, containers, and maximum holding times described in Table II of §136.3(e).

Permit applications that include data which were not generated in compliance with 40 CFR 122 and 136 can be declared incomplete, allowing the permitting authority to and require the permittee to provide additional data. Alternatively, a State or Tribe can use its authority comparable to that under Section 308 of the Clean Water Act to require the permitted facility to collect additional mercury data and provide for permit modification. In seeking new data, EPA recommends that States and Tribes consider requiring additional QA/QC conditions for data collection and analysis. Such measures can minimize or eliminate questions about sample contamination and may be particularly useful where existing data suggests results close to the level of quantification or between the detection level and level of quantification of existing method 245.1.

Appendix D contains examples of additional QA/QC conditions for inclusion in permits. Other suggested sources include the *Guidance on the Documentation and Evaluation of Trace Metals Data Collected for Clean Water Act Compliance Monitoring*, the *Handbook for Analytical Quality Control in Water and Wastewater Laboratories*; and the *Quality Control Supplement for the Determination of Metals at Ambient Water Quality Criteria Levels Using EPA Metals Methods*. EPA currently is evaluating prototype devices that may be capable of producing representative 24-hour samples and evaluating the feasibility of collecting grab samples for subsequent compositing by the laboratory. The results of these efforts will be used to develop new guidance on composite sampling. In the interim, EPA recommends collecting grab samples and then compositing the results mathematically when using new sampling methods.

In addition, States and Tribes should consider requiring analytical methods capable of detecting and quantifying mercury at concentrations closer to the water quality criteria than the most sensitive method currently listed in 40 CFR Part 136, Method 245.1 when more precise information on effluent quality seems desirable. EPA has developed one such method (1631), which employs cold vapor atomic fluorescence [see reference section]. The Method Detection Limit and Minimum Level (also called Level of Quantification) for Method 1631 are 0.05 ng/L and 0.2 ng/L. Use of Method 1631 may be particularly useful where effluent data is below

detection but other data indicates mercury at levels of concern. EPA also recommends that data generated by this method which are submitted by permittees be considered as adequate for regulatory purposes, e.g., making reasonable potential determinations or demonstrating compliance with a WQBEL below the level of quantification. Method 1631 should be used only in conjunction with Method 1669 (clean sampling techniques). EPA maintains a list of laboratories which report their capability to use the new method. See below.

2. Reasonable Potential Determination

a. General: Procedure 5 of the Guidance provides that permitting authorities are required to impose WQBELs for pollutants that cause, have the reasonable potential to cause, or contribute to an excursion above any Tier I criterion or Tier II value. (Note: Since the Guidance included Tier I mercury criteria for aquatic life, wildlife, and human health, Tier II values are not relevant and are therefore not discussed further.)

b. Determining Reasonable Potential With Effluent Monitoring Data: Procedure 5 of the Guidance contains specific procedures for determining whether a discharge causes or has the reasonable potential to cause or contribute to an exceedance of water quality standards. It requires permitting authorities to develop preliminary wasteload allocations for the discharge of pollutants based upon the applicable criteria, using many of the same provisions in Procedure 3 (TMDLs) for developing WLAs such as calculation of background, mixing zones, etc. The permitting authority must then develop preliminary effluent limits consistent with the preliminary wasteload allocations and in accordance with existing State or Tribal procedures for converting wasteload allocations into WQBELs. Using valid, representative, facility-specific effluent data, the permitting authority then determines the projected effluent quality and compares it to the preliminary effluent limitations. In cases where some effluent data are below the level of quantification and other data are above these levels, permitting authorities should use existing State or Tribal procedures to account for these data. EPA's Office of Water is developing national guidance that will address detection and quantification level issues. Where the projected effluent quality value exceeds the projected effluent limit, the permitting authority must develop a water quality-based effluent limit for that pollutant.

Duration and frequency assumptions used to derive the mercury criteria should be accounted for in reasonable potential analyses and in permit limit derivations by use of an appropriate stream design flow when a steady-state model is used. Procedure 3 specifies the 7-day, 10-year (7Q10) stream design flow for chronic aquatic life criteria; the 1-day, 10-year (1Q10) stream design flow for acute aquatic life criteria, the harmonic mean flow for human health criteria, and the 90-day, 10-year flow (90Q10) for wildlife criteria. These recommended design flows are reflective of the duration and frequencies of the water quality criteria in the Guidance. When dynamic modeling techniques are used to determine reasonable potential or to derive limits, the impact of receiving water flow variability on the duration for which and

frequency with which criteria are exceeded is implicitly included in the design conditions if these conditions reflect the desired toxicological effects regime.

c. **Determining Reasonable Potential Without Effluent Monitoring Data:** As discussed above, a permit writer may determine, using the permitting authority's procedures for data evaluation, that the existing effluent data are not suitable for making a reasonable potential determination. Even in the absence of representative effluent data for mercury at a specific facility, a State or Tribe can and should in appropriate situations base a reasonable potential determination upon other valid, relevant, representative information. Other types of information may include dilution, facility type, data from similar facilities, influent and wastewater treatment sludge data, and fish tissue data. In all cases, EPA recommends that the permitting authority also require adequate monitoring to generate reliable effluent data either to establish or verify a reasonable potential finding.

Procedure 5.F.4. states that the permitting authority must find reasonable potential and impose a WQBEL when the geometric mean of a pollutant in fish tissue samples exceed the tissue basis of the Tier I criteria, after consideration of the variability of the pollutant's bioconcentration and bioaccumulation in fish, and the facility discharges detectable levels of the pollutant. In all cases, the permitting authority must exercise its judgment in determining the relevance of any type of data or information to the discharge and receiving water in question.

d. **Consideration of intake pollutants in determining reasonable potential:** Procedure 5 D. in Appendix F provides for a finding of no reasonable potential when the only source of a pollutant of concern in the discharge is the intake water from the same body of water as the discharge and other conditions related to the impact of the discharge are met. EPA recommends that States and Tribes consider an intake pollutant analysis anytime mercury has been detected in the effluent (or a tentative reasonable potential finding has been made on the basis of other information), but there are no known sources of additional contributions of mercury at the facility.

The Guidance leaves to the discretion of States or Tribes what information is needed to make the required demonstrations. One of the conditions for intake pollutant relief is that the facility does not physically or chemically alter the intake pollutant such that the discharge causes increased adverse environmental effects that would not have occurred if the pollutant were left in stream. EPA recommends that States and Tribes consider requiring an evaluation of whether or not the methylmercury concentration increases for facilities with anaerobic conditions.

3. Establishing Permit Limits and Conditions.

a. **General:** After the need for a WQBEL has been established, Procedure 5 specifies how they should be calculated. Essentially, WQBELs are calculated in the same way that projected effluent limits are calculated for determining reasonable potential. Both provisions

rely heavily on the provisions in Procedure 3 related to the development of wasteload allocations. (See Procedure 5.F.1 and 5.A.1.). The provisions common to all three situations include those addressing calculation of background concentrations of pollutants (3.B.9); mixing zones for BCCs (3.C.); deriving TMDLs, WLAs and preliminary WLAs for discharges to open waters of the Great Lakes (3.D.); deriving TMDLs, WLAs and preliminary WLAs, and load allocations for discharges to Great Lakes System Tributaries (3.E.); and Mixing Zone Demonstration Requirements (3.F.). Anticipated future reductions from other sources can be taken into account when developing a WLA in the absence of a TMDL through operation of 3.9.c.iii, which provides that States or Tribes can consider acceptable "available or projected pollutant loading data" when calculating representative background concentrations. The mixing zone provisions described in the above discussion of TMDLs also apply to WLAs in the absence of a TMDL. In those situations where the mixing zone prohibition applies, the effluent limit will be criteria-end-of-pipe. Limits other than criteria end-of-pipe are still possible for existing discharges despite the mixing zone prohibition if the facility qualifies for one of the exceptions to the prohibition. After calculating the WLA, the State or Tribe would use its own procedures for translating WLAs into QBELs. Generally this process involves determining how the duration and frequency of components of WQS will be accounted for in deriving the enforceable permit limit.

b. Limits Based on "No Net Addition"/Intake Credits: When the receiving water already exceeds criteria, a facility's WLA calculated using the procedures in 5.F.2. is likely to be less than background levels for that pollutant. When conditions for intake pollutant relief are met as described in Procedure 5.D, except that there are known additional contributions of mercury to the wastestream at the facility, dischargers may still be eligible for relief in the form of "no net addition" limits under Procedure 5.E. This approach for developing QBELs operates independently of the other Procedure 5 provisions for developing WLAs and QBELs in the absence of a TMDL. The "no net addition" approach allows the discharger to discharge the amount of mercury in its intake waters but not an additional amount. Thus it relieves the discharger from having to remove mercury from the background water that may originate from other sources, but requires the discharger to eliminate any incremental amount of mercury in the discharge that originates at the facility.

"No net addition" limits are available only if the levels of the pollutant in the background water of the discharge exceed the most stringent applicable criteria. Background concentrations are determined using Procedure 3.B.9. of Appendix F. This procedure specifies how detection level considerations are to be handled in calculating background concentrations. Where the available data sets consist of values above and below the method detection level, States and Tribes have flexibility to evaluate the data using commonly acceptable statistical methods. [Procedure 3.B.9.d.i.] Examples of commonly acceptable statistical methods include those in Chapter 14 of *Statistical Methods for Environmental Pollution Monitoring* (Richard O. Gilbert; published by Van Nostrand Reinhold) and *Truncated and Censored Samples* (A. Clifford Cohen; published by Marcel Dekker). Where a State or Tribe has determined, based on an evaluation of available data, to use default values rather than a statistical approach, EPA recommends using

default values of one-half the method detection level for data points reported as below the method detection level, and the mid-point between the detection level and quantification levels for data points above the method detection level but below the quantification level. Where all data sets or categories of data judged by the permitting authority to be adequate are below the method detection level, all data for that pollutant shall be assumed to be zero. [Procedure 3.B.9.d.ii.]

If a discharger is eligible for "no net addition" limits under the intake credit procedure as described above, the permitting authority has discretion in developing the most appropriate conditions for establishing the limit and assessing compliance. The SID discusses two alternatives: (1) establishing a numerical limit based the representative background levels of the intake water source; or 2) establishing a limit of no change between intake and effluent. Regardless which option is chosen, the requirements of Procedure 8 (WQBELs Below the Level of Quantification) should be applied if background values derived under Procedure 3.B.9.d. are below the level of quantification.

"No net addition" limits will be available for new and existing discharges of mercury until March 23, 2007. After that time, limits will be set at criteria-end-pipe, unless the authorized by a TMDL and the discharge qualifies for one of the exceptions to mixing zone ban, as discussed in section III.B.2., above. EPA limited the availability of "no net addition" intake credits for setting limits to ten years, i.e, until March 23, 2007, when States are to adopt and begin implementation of the Guidance as a way to encourage TMDLs. Thereafter, "no net addition" credits would be available only if authorized by a TMDL. In recognition of this, the Council of Great Lakes Governors, in its Statement of Principles dated February, 1996, committed to do TMDLs prior to March 23, 2007. EPA and the States recognize that progress in developing TMDLs should be reevaluated at "mid-point" to determine if the phase-out of no net addition limits remains appropriate.

c. Limits Below the Level of Quantification.

WQBELs for mercury will sometimes be set below the level of quantification, especially when mixing zones are not allowed, e.g., for new discharges of BCCs or where the receiving water already exceeds criteria. This is because Methods for Chemical Analysis of Water and Wastes (EPA -600/4-79-020) Method #245.1 for Manual Cold Vapor Analysis measures organo-mercury compounds and methyl mercuric chloride in flameless atomic absorption spectrophotometry, with a detection level (minimum level, based on lowest calibration point) of 0.2 µg/L. In contrast, the Great Lakes mercury criterion for human health is 1.8 ng/L; the acute aquatic criteria, 1.44 µg/L dissolved; the chronic aquatic criteria, 0.77 µg/L dissolved; and wildlife criteria is 1.3 ng/L.

Procedure 8 of the Guidance provides that when permit limits are set below the level of quantification, the permit must contain the WQBEL as calculated. The Guidance also states that the permit should specify the quantification level for the required analytical method and how

compliance with the limit will be assessed, including how values below the level of quantification will be considered in calculating average values. The Guidance leaves averaging procedures to State and Tribal discretion. To promote national consistency in reporting monitoring results and to improve the quality of data in the Permit Compliance system(PCS) database, EPA is planning to issue guidance which will address the reporting of monitoring results which are below analytical quantification and detection levels. This guidance, which is currently under development, will apply to all pollutant parameters which are set below quantification. The detection level guidance will include recommendations for calculating average values, reporting values on Discharge Monitoring Reports and in PCS, and determining appropriate enforcement responses.

d. Pollutant Minimization Plans

In addition, permittees must develop a pollutant minimization program (PMP) for pollutants with WQBELs below the level of quantification. The PMP is designed to proceed toward the goal of maintaining all sources of the pollutant to the permittee's wastewater collection system at levels below the WQBEL, with the overall goal of maintaining the final effluent at or below the WQBEL. The PMP requirements in the Guidance do not specify what control measures, if any, a discharger will need to implement in order to ensure that the effluent discharged to the receiving water actually achieves the WQBEL. However, a discharger is required to develop a control strategy as part of the PMP. The discharger works with the permitting authority to determine what control measures are appropriate in any particular case. States and Tribes can consider cost-effectiveness when identifying control measures to be implemented. Once these cost-effective control measures have been determined, implementation of those measures is an enforceable requirement of the permit. PMPs are subject to revision and EPA envisions that the implementation of PMPs will be an iterative process where the annual results of the PMP are used to modify subsequent updates of the PMP as appropriate.

EPA anticipates that the PMP will serve to emphasize the opportunities afforded by source reduction up front, rather than by traditional reliance on end-of-pipe treatment. While Procedure 8 does not prohibit treatment as an alternative for reducing mercury levels in the effluent, EPA notes that a pollution prevention approach for reducing mercury may well have the added advantage of reducing mercury releases to other media. Because mercury releases from other media are known to impact water quality, any reduction in mercury releases has the potential to benefit point sources by reducing mercury levels in a facility's source and/or receiving water. Pollution prevention also plays a significant role in other implementation procedures under the Guidance. The first step of an antidegradation analysis for BCCs is to identify any and all cost-effective pollution prevention alternatives that might eliminate or reduce the proposed significant lower of water quality. Similarly, a State or Tribe can grant an exception to the mixing zone prohibition only if feasible alternative control strategies, including pollution prevention, do not exist. Clearly, EPA regards pollution prevention as an important and effective element in the control of mercury.

A pollution prevention approach is also consistent with the many state and local efforts, often voluntary, already undertaken in the Great Lakes States to reduce mercury releases to the environment. Appendix A lists many of these efforts. The Blueprint for Mercury Elimination is a notable, recent resource for developing a comprehensive approach for identifying and evaluating sources of a mercury to a system and devising reduction strategies. The Blueprint is informative for both POTWs and industry. EPA is also committed to assisting States, Tribes and the regulated community in their efforts to share information on mercury reduction strategies. EPA encourages pollution prevention as a major element of any mercury reduction strategy, whether or not undertaken as part of a PMP or other regulatory requirement.

EPA recognizes that a permittee may demonstrate that its effluent is below the permit limit through means other than effluent monitoring using existing Part 136 methods (for example, see discussions on new analytical methods). When this is accomplished to the satisfaction of the permitting authority, the permit need not require a PMP. In this situation, EPA recommends that the State or Tribe consider requiring that the method used by the permittee to demonstrate compliance be used as the basis for compliance monitoring in the permit. Under Procedure 8.C., "alternative" monitoring to assess pollutant levels in the effluent may be required even if it is not the specified basis for evaluating compliance with permit conditions.

e. New Analytical Methods

In the future, EPA expects to promulgate under 40 CFR 136 analytical methods for mercury that are more sensitive than Method 245.1. Such methods will allow dischargers and EPA, States, and Tribes to obtain far more precise information on low levels of mercury in discharges from point sources and in ambient water. The existing Part 136 method continues to be valid for regulatory purposes, even though it may not detect all possible situations where mercury is of concern in an effluent. Certainly, States and Tribes can rely on data submitted by the permittee and certified to be true and accurate to the best of the permittee's knowledge. EPA also believes that a State, Tribe or permittee could justify using data generated by the new analytical method (Method 1631) for regulatory purposes, based on EPA's confidence in the soundness of the new method. For example, a permitting authority, in determining whether a WQBEL is needed, may decide to require use of Method 1631 to further evaluate an effluent where the current method does not detect the presence of mercury in the effluent, but other information such as detectable levels in the wastewater treatment biosolids, suggests that mercury could be present in the effluent at levels of concern. (As before, permitting authority can also rely on non-effluent data to make reasonable potential determinations).

Availability of laboratories that are capable of using the new methods is a factor States or Tribes may consider when determining whether to require use of the new method before it is required by its inclusion in Part 136. (Compliance schedules to provide time to secure laboratory services is also a possibility.) EPA maintains a partial list of commercial labs which report using the new methods, including several in the Great Lakes basin. To obtain this list of labs, as well as

the new methods, contact Ben Honaker of EPA's Engineering and Analysis Division at (202) 260-2272.

IV. ANTIDEGRADATION

A. INTRODUCTION

States and Tribes water quality standards must include an antidegradation policy. At a minimum, an antidegradation policy ensures that existing uses of waters are protected, that water quality in high quality waters is protected unless a lowering of water quality is necessary to accommodate important social and economic development and that water quality in outstanding national resource waters is maintained and protected. The antidegradation provisions of the Guidance mandate specific procedures for implementing antidegradation that are intended to protect the Great Lakes System from new and increased loadings of BCCs. The Guidance supplements existing antidegradation regulations at 40 CFR 131.12 by providing more detailed information about how to implement the antidegradation requirements for BCCs.

As with other elements of States' and Tribes' water quality standards, the NPDES permit program is one of the primary mechanisms through which a State's or Tribe's antidegradation policy is implemented. The antidegradation implementation procedures contained in the Guidance are intended to function within the context of an NPDES program. Dischargers contemplating an action expected to result in an increased loading of mercury will need to contact their permit issuing authority for authorization as required by their discharge permit. As a result, permitting agencies can expect to play a significant role in antidegradation implementation.

B. OVERVIEW OF GUIDANCE ANTIDEGRADATION PROVISIONS

1. Protection of Existing Uses

Appendix E of the Guidance and existing Federal regulations at 40 CFR 131.12 require that water quality necessary to support existing uses be maintained and protected. The Guidance adds that where designated uses are impaired, further lowering of water quality due to the pollutant or pollutants causing the impairment is not permitted. (For example, impairment could be determined by an exceedance of the water quality criteria.) In brief, further lowering of water quality for the impairing pollutant is not allowed in nonattained waters; the provisions for an antidegradation review are not applicable in this situation.

2. Protection of High Quality Waters

Appendix E requires identification of high quality waters on a pollutant by pollutant basis. Thus, an individual water body may be considered high quality for one pollutant and not for another. An antidegradation review is required any time there will be an action lowering water

quality for any pollutant currently above fishable/swimmable, even if water quality criteria for other pollutants are violated in the water body.

An antidegradation review is required any time there will be an action significantly lowering water quality. The Guidance defines any increase in loading of a BCC (including mercury) as significant. The Guidance provides examples of the types of activities requiring an antidegradation review. These include: construction of a new regulated facility requiring a new discharge permit; modification of an existing facility such that a new discharge permit is required; addition of a new source of untreated or pretreated effluent containing or expected to contain BCCs to an existing wastewater treatment works; or a request for an increased permit limit. The Guidance also requires that permits include conditions which ensure that significant lowering of water quality does not occur without advance notice to the State or Tribe and that an antidegradation review is undertaken where appropriate.

The antidegradation review focuses on two questions: is the lowering of water quality a necessary result of the proposed activity; and will the proposed activity support important social and economic development in the area affected by the lowering of water quality? To answer the first question, a discharger must investigate pollution prevention and improved treatment technology as a means of reducing or eliminating the expected increased loading of BCCs. To answer the second question, a discharger must identify the social and economic development and benefits that will be foregone if the lowering of water quality is not permitted. The State or Tribe may allow all or part of the proposed lowering as necessary to accommodate the important social and economic development if it determines that a lowering of water quality is both necessary and will support important social and economic development (assuming of course, that the existing and designated uses will continue to be maintained and protected).

3. Outstanding National Resource Waters

Water quality in a water body identified as an Outstanding Natural Resource Water (ONRW) must be maintained and protected. Only short-term and temporary reductions in water quality are permissible in an ONRW.

V. SUMMARY

The Guidance contains a number of mechanisms for adjusting point sources controls that directly or indirectly authorize States or Tribes to account for nonpoint source contributions to mercury impairment of the Great Lakes system. In the short-term, use of the mechanisms can help to minimize the need of requiring reductions from point sources in some cases where multiple sources are involved. Ultimately, however, comprehensive reduction of mercury from other anthropogenic sources will be needed so as to maintain and achieve water quality standards.

*** *Public Review Draft* ***

APPENDICES

- A. Summary of Other EPA, State, and Tribal Mercury Initiatives and Programs [Forthcoming]
- B. Implementation Flow Chart
- C. Developing Site-Specific Modifications To Criteria for Mercury
- D. Recommended QA/QC Requirements
- E. List of Resources/Contacts [Forthcoming]

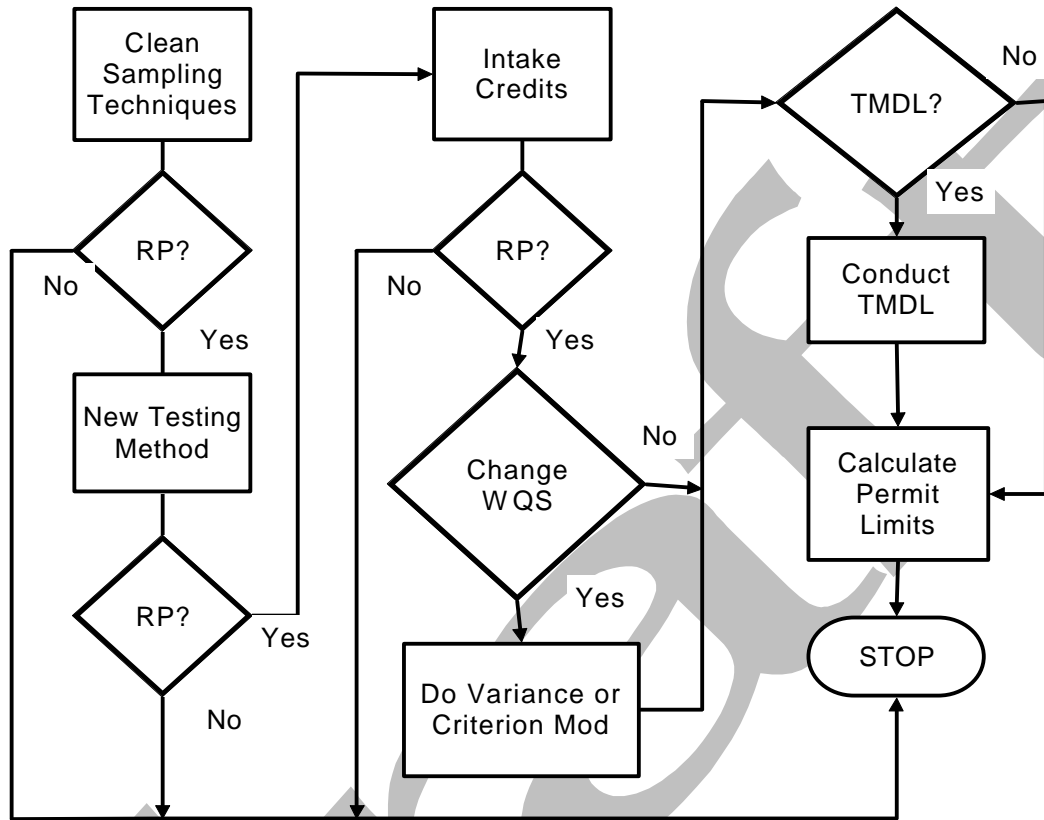
*** *Public Review Draft* ***

APPENDIX A
SUMMARY OF OTHER EPA, STATE, AND TRIBAL MERCURY INITIATIVES AND
PROGRAMS

[Under Development]

Draft

APPENDIX B
IMPLEMENTATION FLOW CHART



APPENDIX C DEVELOPING SITE-SPECIFIC MODIFICATIONS TO CRITERIA FOR MERCURY

BACKGROUND

The Guidance for the Great Lakes System ("Guidance") established an acute and chronic aquatic life criteria for mercury(II) expressed as dissolved mercury concentrations of 1.44 $\mu\text{g/L}$ and 0.77 $\mu\text{g/L}$, respectively. The human health mercury criteria was 1.8E-3 $\mu\text{g/L}$ expressed as total mercury and the wildlife mercury criteria was 1.3E-3 $\mu\text{g/L}$ expressed as total mercury. The Guidance allows for more or less stringent modification of these criteria on a site-specific basis to reflect local environmental conditions. More stringent aquatic life, wildlife, and human health criteria can be derived on a site-specific basis to provide an additional level of protection, pursuant to authority reserved to the States and Tribes under CWA section 510. Less stringent site-specific modifications can also be derived if they are protective of designated uses and aquatic life, wildlife, or human health and submitted to EPA for approval. In addition, any site-specific modifications that result in less stringent criteria are required to be based on a sound scientific rationale and would be unlikely to jeopardize the continued existence of endangered or threatened species listed or proposed under section 4 of the Endangered Species Act (ESA) or result in the destruction or adverse modification of such species critical habitat. As with any site-specific criterion modification, implementation must ensure that downstream uses are protected.

This Appendix provides a brief overview of mercury speciation and cycling in surface waters, a discussion of the components of the mercury criteria derivation which can be modified site-specifically, and the different approaches available for modifying the bioaccumulation factor (BAF), which is the component of the mercury criteria most likely to be modified on a site-specific basis for human health and wildlife.

MERCURY SPECIATION AND CYCLING

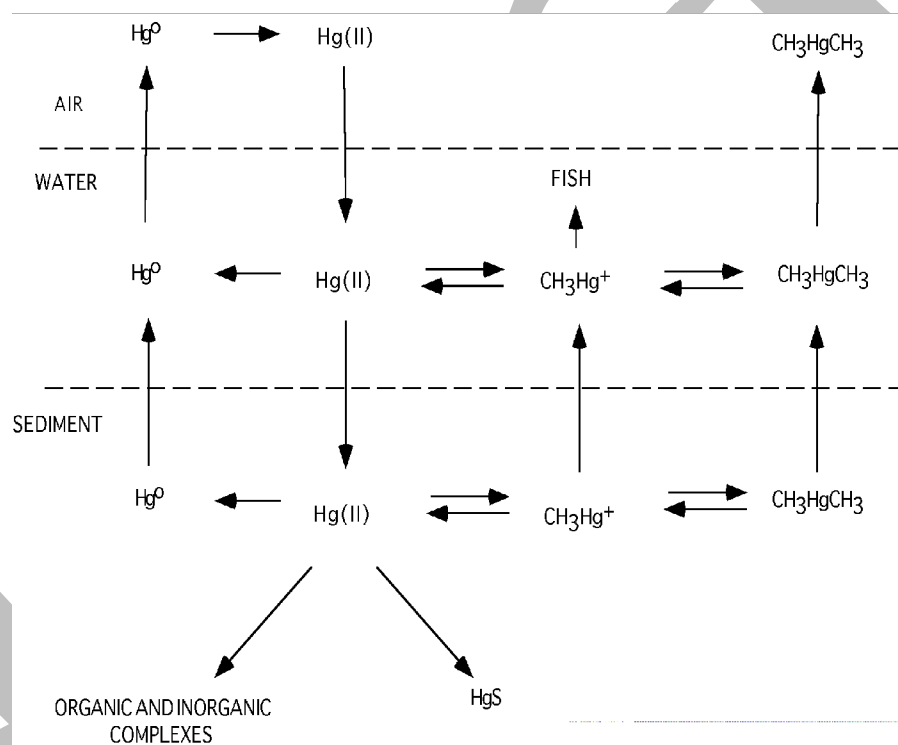
Because of the complexity of mercury chemistry in aquatic ecosystems, it is important to have a basic understanding of mercury speciation and cycling in surface water bodies. Figure 1 provides a simplified version of mercury cycling in the environment and the major transformations between the different forms of mercury (for more detailed reviews on mercury cycling see Winfrey and Rudd, 1990; Parks 1988; and Driscoll et al. 1994).

Mercury can exist in three states (elemental mercury - Hg^0 , mercury(I) - Hg_2^{2+} , and mercury(II) - Hg^{2+}) and can react with other chemicals to form inorganic compounds (mercuric chloride - HgCl_2) and organic compounds (e.g., methylmercury - CH_3Hg^+ and dimethylmercury - $(\text{CH}_3)_2\text{Hg}$). Mercury enters surface waters as Hg^0 , Hg^{2+} , or methylmercury. Once in aquatic systems, mercury can exist in dissolved or particulate forms and can undergo the following transformations (Lindqvist et al, 1991; Winfrey and Rudd, 1990)

- Hg^{2+} can be reduced to Hg^0 .

- Volatile Hg^0 can be released to the atmosphere.
- Atmospheric Hg^0 may be oxidized to Hg^{2+} , and may be deposited/redeposited to surface waters.
- Hg^{2+} can be methylated in sediments and the water column to form methylmercury.

Figure 1: *Biogeochemical Cycling of Mercury in Freshwater Lakes* (from: Winfrey & Rudd, 1990)



The predominant forms of mercury in surface waters are inorganic mercury(II) and methylmercury. Methylmercury is the mercury compound thought to be of most concern for wildlife and humans because methylmercury bioaccumulates and biomagnifies in aquatic food webs to a greater extent than any other form of mercury (Watras and Bloom, 1992) and because of its toxicity to birds, mammals, and aquatic organisms. Several studies have indicated that the vast majority (greater than 95%) of mercury in fish tissue is methylmercury (Grieb, 1990; Bloom, 1992; Southworth et al., 1995).

The dominant factor affecting the uptake of mercury in fish is the fraction of total mercury available in the methylmercury form. Methylmercury conversion, although once believed to take place almost entirely in the sediments via biotic production by sulfate reducing bacteria, is now recognized as occurring biotically at the sediment water interface, in the water column, on slime

layers and in the intestines of fish, and possibly abiotically via reduction of mercury(II) by humic acids (Winfrey and Rudd, 1990). The main factors that influence the net production of methylmercury from total mercury in surface waters include:

pH: Numerous researchers have linked elevated mercury concentrations in fish to poorly buffered, low pH systems (Lindqvist et al. 1991; Wiener et al. 1990; Sorensen et al. 1990; Bloom et al., 1991; Watras and Bloom, 1992);

Dissolved organic carbon: The effect of DOC on mercury accumulation in fish is not clear, with some research indicating that DOC inhibits methylation and others indicating a possible increased persistence of mercury(II) or methylmercury in the water column, thereby increasing methylmercury accumulation in fish (Winfrey and Rudd, 1990; Hudson et al., 1994; USEPA, 1993).

Sulfate-reducing bacteria: Several researchers have demonstrated that in anoxic sediments, the principal bacteria responsible for methylation of mercury(II) are sulfate-reducing bacteria (Kerry et al., 1991; Compeau and Bartha, 1985 as cited by Winfrey and Rudd, 1990). However, data on the effect of sulfate on methylmercury production is contradictory with Kerry et al. (1991) finding no significant stimulation of methylmercury production and Gilmour et al. (1992) showing stimulation of methylmercury production with increasing sulfate concentrations.

Fish-specific characteristics: Field data on mercury accumulation in fish show a positive correlation between fish size, age, length, and weight and mercury tissue concentration (Lindqvist et al. 1991; Grieb et al. 1990; Sorensen et al. 1990).

Lake stratification: Several researchers have shown an effect of lake stratification on total and methylmercury concentrations at different depths in Little Rock Lake (Bloom et al., 1991).

Many of the factors mentioned above are related to each other and distinguishing between the effect of different lake characteristics on the bioaccumulation of mercury in fish can be difficult due to these confounding factors (Spry and Wiener, 1991). However, these are important factors that need to be considered when designing studies for determining BAFs on a site-specific basis.

SITES-SPECIFIC CRITERIA MODIFICATIONS

The site-specific modifications for aquatic life in the Guidance are consistent with the existing guidance developed in Chapter 3 of the U.S. EPA Water Quality Standards Handbook, Second Edition, Revised (USEPA, 1994) and are not discussed here.

The Guidance focussed on the development of less stringent site-specific wildlife criteria when a site-specific BAF could be developed which is lower than the system-wide mercury BAF (27,900 for trophic level 3 and 140,000 for trophic level 4). EPA also considered allowing less stringent modifications to the wildlife criteria based on site-specific distributions of wildlife species, and their associated dietary habits, but believes that a justification of a less stringent site-specific modification based on these factors will be difficult to make because the representative species listed in the Guidance were not selected to be the only species targeted for protection; rather, they were selected to exemplify the most exposed wildlife species resident or incidental in the basin. Therefore, for a specific site the mercury criterion would still protect other highly exposed wildlife species from adverse effects even if one or more of the representative species are not found at that site. However, EPA did not preclude in the Guidance the ability to calculate site-specific modifications to wildlife criteria using different set of wildlife species or exposure assumptions.

With respect to human health criterion, the Guidance focussed less stringent site-specific modifications where local fish consumption rates are lower than the rate used in deriving human health criteria (15 grams/day) using a well conducted fish consumption survey or a site-specific BAF is derived which is lower than that used in deriving human health criteria (27,900 for trophic level 3 and 140,000 for trophic level 4). Other exposure parameters such as drinking water consumption rate, body weight and incidental ingestion rate can fluctuate on a population basis, but were not considered parameters likely to change on a site-specific basis. With regard to toxicological assessments, EPA does not believe there are likely conditions under which a site-specific toxicological assessment for mercury can be made. For example, to make a site-specific toxicological assessment, it would have to be shown that a particular human population at a specific site was more or less sensitive to mercury due to genetic predisposition or site-related conditions which mitigate or enhance the toxicological effects of mercury. Again, EPA believes making such a showing is highly unlikely and probably implausible.

EPA believes, on the other hand, that it is conceivable that there might be isolated tributaries and populations of people who do not consume as much fish as the rate presented in the Guidance. Such a demonstration would likely be difficult to make, due to the transience of people in the Great Lake area, but if a State or Tribe can demonstrate, based on data, that a group of people who are the exclusive users of a waterbody has a significantly lower fish consumption rate than 15 g/day, they may apply that lower rate in developing their human health criteria for that waterbody. The States and Tribes must ensure that fish migration from the waterbody in question will not lead to increased exposure to other human populations. The State or Tribe must also demonstrate that the specified waterbody is not associated with a known or anticipated group of individuals who may consume more fish, such as a sport or subsistence angler population. To ascertain such information, the State or Tribe must conduct a site-specific fish consumption survey. When determining a site-specific fish consumption rate, a site-specific fish lipid percentage must also be determined. For information on how to conduct a fish consumption survey and how to analyze the results, refer to the EPA document "Consumption Surveys for Fish

and Shellfish. A Review and Analysis of Survey Methods". Feb. 1992. EPA 822/R-92-001 (USEPA, 1992).

In summary, the BAF is the most likely component in the derivation of wildlife and human health mercury criteria that could be changed on a site-specific basis to allow less-stringent criteria. The other factors such as body weight and toxicological data are not as amenable to site-specific modifications. The mercury BAF in the Guidance was designed to represent a reasonable estimate of the bioaccumulation potential of mercury for the entire Great Lakes system. EPA recognizes that because of different environmental conditions, the mercury BAF maybe too high or too low for a particular site or area. Because of this, EPA believes that mercury BAFs different than those used in the Guidance could be justified on a site-specific basis.

The development of site-specific BAFs can be accomplished in one of three ways: 1) develop a site-specific field-measured BAF; 2) use the approach in the final Guidance; or 3) use other appropriate site-specific models such as the Mercury Cycling Model. When using these approaches, it is important that site data be used for all parameters, unless default data can be shown to represent local conditions. All of these approaches are discussed below.

FIELD-MEASURED BAFS

The BAF is defined in the Guidance as the ratio of a substance's concentration in tissue of an aquatic organism to its concentration in the ambient water. The BAF definition is applicable to the development of site-specific criteria. Because of the importance of collecting accurate tissue and ambient water concentrations when deriving field-measured BAFs, it is important that the best quality data be used. To assure the best quality data are used, several important elements should be considered when developing a site-specific mercury BAF. These include: the selection of appropriate consumed aquatic species; field procedures for sampling design, sample collection, and sample handling of fish samples, water samples, sediment samples, and other water quality characteristics; and laboratory procedures for sample handling and sample analyses. Each of these will be discussed briefly below.

Tissue Concentrations

When deriving a site-specific BAF it is important to collect fish samples from fish at or near the top of the aquatic food chain (i.e., in trophic levels 3 and/or 4). For the Great Lakes, EPA has identified several bottom feeding species (common carp, channel catfish, and white sucker) and predator species (white bass, smallmouth bass, walleye, muskellunge, chinook salmon, lake trout, brown trout, and rainbow trout) as examples of species that should be considered when conducting sampling to characterize the concentration of various chemical contaminants including mercury (USEPA, 1995 - Sampling Volume 1).

EPA's Guidance for Assessing Chemical Contamination Data for Use in Fish Advisories: Volume 1: Fish Sampling and Analysis Second Edition contains detailed information on sampling design, sample collection, and sample handling for collecting fish samples and on laboratory procedures for sample handling and sample analyses. Because of the detail provided in this document no further discussion of this area will be provided here. When designing a plan for determining a site-specific BAF for mercury, individuals should consult this document.

Ambient Water Samples

Because mercury concentrations in ambient water are generally very low, water samples must be collected with care to avoid contamination. Bloom (1995) provides a description of the current methods for sample collection and analysis of mercury in ambient water and fish. His discussion focuses on the methods and analytical considerations necessary for the accurate and precise determination of total mercury and methylmercury in aquatic organisms and the ambient waters.

Other water quality characteristics

In addition to fish tissue samples and ambient water samples, it is also important to collect information concerning other factors that might influence the bioaccumulation of mercury such as pH, dissolved organic carbon concentration, and sulfate concentrations.

MODIFICATION OF MERCURY BAF USING Guidance APPROACH

To understand how the mercury BAF in the Guidance could be modified, it is important to first understand how the BAF was derived. The mercury BAF in the Guidance was based on a weighted average bioconcentration factor (BCF) multiplied by biomagnification factors (BMFs) and the percent of total mercury occurring as methylmercury in fish tissue. The mercury BAF was derived using the following information (see USEPA, 1995 for a more detailed discussion of the data used).

$$\text{BAF} = (\text{Weighted Average BCF})(\text{BMFs})(\% \text{ methylmercury in fish})$$

- Weighted Average BCF: The percent of total mercury occurring as methylmercury in water was assumed to be 17 percent. The BCF for inorganic mercury is 2,998 and the BCF for methylmercury is 52,175. Thus, the weighted average BCF is $(0.17)(52,175) + (0.83)(2,998) = 11,358$.
- Biomagnification factors: BMFs were 2.00 (trophic level 1 to 2), 1.26 (trophic level 2 to 3) and 5.00 (trophic level 3 to 4).

- % methylmercury in fish: The estimated percent of total mercury occurring as methylmercury in fish was assumed to be 97.5 percent.

Based on this information the BAFs for trophic level 3 and 4 were derived as follows:

$$\text{BAF trophic level 3} = (11,358)(2.00)(1.26)(0.975) = 27,900$$

$$\text{BAF trophic level 4} = (11,358)(2.00)(1.26)(5.00)(0.975) = 140,000$$

Using the approach in the Guidance, the mercury BAF can be modified on a site-specific basis by adjusting:

- 1) the percent of total mercury occurring as methylmercury in water;
- 2) the BCFs for inorganic mercury or methylmercury;
- 3) the BMFs for the different trophic levels; and/or
- 4) the percent of total mercury occurring as methylmercury in fish.

However, if this approach is used it is important that all of the parameters be modified based on site-specific data or EPA's default parameters if supported by local data. EPA does not believe it would be appropriate to change one parameter that would lower the BAF on a site-specific basis and not change other parameters that might raise the BAF.

MODIFICATION OF BAF USING OTHER METHODS

A site-specific BAF for mercury may also be derived using the Mercury Cycling Model (MCM) developed as part of the Mercury Temperate Lakes Program sponsored by the Electric Power Research Institute and the Wisconsin Department of Natural Resources (Hudson et al. 1994). The MCM model dynamically simulates the transport and transformation reactions in each of the main lake compartments based on principles of mass conservation, chemical equilibria and kinetics, and ecosystem bioenergetics (Leonard et al. In press). Required input parameters include lake physical characteristics, water quality parameters, atmospheric and other inputs, and biomass characteristics. If this model is used, it is important that the input parameters are site-specific and not default values.

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APPENDIX D QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) RECOMMENDATIONS

NOTE: EPA currently is developing new QA/QC and sampling protocols. These will be forthcoming as additional methods and guidance and/or as revisions to the current Part 136 analytical methods for metals and anticipates proposing those revisions in Spring 1997. This is an evolving area and EPA encourages States and Tribes to follow developments and consider new techniques as they become available. In the meantime, EPA thinks it is important to begin incorporating QA/QC requirements now to ensure the best possible data for making decisions about mercury controls. This Appendix contain recommendations for accomplishing this interim goal. Method 1669 is also recommended for consideration.

Suggested QC Items for Review & Inclusion in NPDES Permits

The permittee is required to show the validity of all data by requiring its laboratory and sampling personnel to adhere to the following minimum quality assurance practices:

1.Blanks:

Rinsate or Equipment Blanks ("Comprehensive" Blanks): DI water passed through sample collection equipment. First performed in the laboratory and analyzed to verify acceptable contamination control before the equipment is used for sampling. Also taken in the field with each set of samples, and acidified under the same conditions as the samples using the same acid. This blank when treated in the laboratory with all the steps required for sample analysis should indicate if contamination is involved in any aspect of the mercury sampling plus analyses. The following additional blanks (e.g., field, method, and reagent) can help isolate sources of contamination for remedial action.1, 2, 3

Field Blanks: DI water in a typical sample container acidified under the same conditions as the samples using the same acid. Contamination detected in this blank, if not detected in method blanks or reagent blanks, indicates a contamination occurring during sampling (poor technique, contaminated containers, acid).1, 2, 200.7, 200.8, 200.9 - EPA 94

Trip Blanks: DI water in a typical sample container acidified in laboratory and transported under the same conditions as the samples. Trip blanks are more important for volatile analities, e.g., mercury. Contamination detected in this blank, if not detected in the method or reagent blank suggests contamination during the transport process.

Method Blanks: Minimum of two (to assess systematic versus random contamination) carried through all laboratory sample preparation procedures (digestion) and analysis in the laboratory. Contamination in the method blank is associated with conditions in the laboratory. If the reagent blank is not contaminated, this would indicate problems during

the digestion step, e.g., hood fallout, dirty beakers or watch glasses, etc. **1, A single Method Blank is required by 3110, 3111, 3113, 3120 - SM 18; METALS - EPA 79/83; 200.7 - CFR 136; 200.7, 200.8, 200.9 - EPA 91 & EPA 9**

Reagent Blank: (Calibration Blank) Prepared with DI water and acid matched to samples. Contamination in the reagent blank is associated with conditions in the laboratory. If the method blank is found to be contaminated to the same level, this would indicate problems with the lab pure water or the acids. 1, 3110, 3111, 3113, 3120 - SM 18; METALS - EPA 79/83; 200.7 - CFR 136; 200.7, 200.8, 200.9 - EPA 91 & EPA 94

Blank Interpretation:

As indicated above, the various blanks can help pin point the source/s of the contamination (lab or sampling, etc.). In general, blank results greater than 10% of the sample result indicates "not acceptable" contamination. One exception to this 10% rule is in the case of "not detect" results for samples with elevated blanks. In this exception, if all other QC items are within control (QC "acceptable") then the sample results would be reportable ("acceptable"). Another exception to this 10% rule is for reagent blanks. Since a reagent blank is under the direct control of the laboratory and could be easily reanalyzed and directly affects the quality of the calibration--a reagent blank should not exceed the MDL. Laboratory analyses should be stopped until the source of the elevated reagent blank is eliminated.

If blanks exceed the 10% rule and indicate a laboratory problem, corrective action should be performed and reanalysis should be performed (assuming that the samples are within the holding times and properly preserved). If the problem cannot be resolved within the holding time of the samples the results are flagged as already described.¹

If blanks exceed the 10% rule and the problem is indicated as a sampling problem then the results are flagged as already described.

Plan to Reduce Blank Burden:

Initially all of the blanks listed above are to be collected. Method blanks are prepared (since it cannot be prepared correctly after-the-preparation of the other samples). All of these blanks are stored in a secure laboratory setting (with controlled access and free from contamination). If the analysis of the equipment/rinsate blank and the reagent blank indicates no contamination (10% rule) then the other blanks need not be analyzed. If contamination is detected in the reagent blank (analyzed during instrument calibration), the problem must be corrected before additional analysis. If contamination occurs in the equipment/rinsate blank, then the other blanks must be analyzed to help isolate and correct the problem. If contamination problems are not encountered, the types of blanks collected can be reduced. Again, the minimum number of blanks includes the equipment/rinsate blank and the reagent blank.

In addition, it is suggested that grab samples may reduce the potential for contamination. If grab samples cannot be taken (composite specified on permit), the equipment must be tested and certified free of contamination in the laboratory.²

2. Linear Working Range & Calibration Established:

The standard curve (at least 3 standards and a reagent blank) must be generated daily. 1, 3111, 3113 - SM 18; 200.9 - EPA 91 & EPA 94; 4 standards required by METALS - EPA 79/83

Quantifiable unknowns must be bracketed by standards 3111, 3113 - SM 18; METALS - EPA 79/83

The standards must contain the same types and quantities of acids as the samples analyzed. 3110, 3111, 3113, 3120 - SM 18; METALS - EPA 79/83; 200.7 - CFR 136; 200.7, 200.8, 200.9 - EPA 91 & EPA 94

A reference material of known concentration from a source other than the standards must be successfully analyzed before beginning analyses each day 200.8 & 200.9 - EPA 91; 3020 & 3120 - SM 18

Microliter pipets used to prepare standards must be calibrated **(at least monthly)**.

These requirements provide mechanisms for confirming the accuracy of the standard curve before unknowns are analyzed and provide documentation of the accuracy of that curve to accompany the sample results.

3. DI water, acids and reagents used for preparation of standards and reagents must result in reagent blanks \leq the MDL. ²

The reagent blank must be controlled to avoid false positives and falsely elevated readings.

4. For total metals (total recoverable) samples are correctly preserved and digested prior to analysis (40 CFR Part 136).

Improper preservations and digestion or lack of digestion will result in a loss of metals. The resulting data will be biased low and are not consistent with program requirements. ²

5. Samples for dissolved metals are filtered on site prior to acidification (40 CFR Part 136). Note: the details of the filtration device/procedure are critically important and will have to be specified 2

Filtration studies have been conducted which indicate that more criteria than filter type (i.e., filter size, sample volume, filter treatment, pressure vs vacuum) must be defined in order to avoid bias in the amount of dissolved metals that pass through the filtration device for analysis. The time factor remains critical as the dissolved phase is dynamic and changes with time; filtration must take place on site as soon as possible after sample collection for dissolved metals to be representative of the sample as originally collected. 2

6. Background Correction and Interement Correction :

For Flame AAS, Background Correction must be used for all wavelengths less than 350 nm (METALS - EPA 79/83; 3111 - SM 18). For Graphite Furnace AAS it must be used for all work (METALS - EPA 79/83; 200.9 - EPA 94) (spike recovery analysis will not detect background contribution, and the Method of Standard Additions (MSA) will not correct for it).1

Interement Corrections and Background Corrections must be documented and are verified for ICP-AES. Concentrations of interfering elements used to perform corrections on reportable data must fall within the documented linear range (200.7 - CFR 136, 200.7 - EPA 91 & EPA 94; 3120 - SM 18).

Contribution from Background and from Interement Interferences can cause positive bias (falsely high results) of undetermined magnitude. Spike recovery analysis will not detect background contribution, and the Method of Standard Additions (MSA) will not correct for it.

7. Matrix modifiers are to be used to minimize matrix effects and improve performance (EPA listed or instrument manufacturer's recommended) (1, METALS-8, EPA 79/83; 3113 - SM 18) (Palladium modifier required - 200.9 EPA 91 & EPA 94).

Matrix modifiers serve to keep the element of interest in a less volatile form and/or make background-producing salts more volatile. This allows volatilization of the salts at a lower temperature while the element of interest is retained until the determinative step (atomization). The result is that matrix effects are reduced. Successful spike recovery (85-115%) or successful application of the Method of Standard Additions (MSA) indicates that an appropriate matrix modifier was used.

8. Check standards with concentrations at the mid-point of the calibration standards or at the method-required level are successfully analyzed (within 10% or 5% of the "true value" - see criteria in individual methods) at the method-required frequency (20 samples for furnace (METALS - EPA 79/83), 10 samples for ICP-AES (3120 - SM 18; 200.7 - CFR 136, EPA 91 & EPA 94), 10 samples for STGFAA (200.9 - EPA 91 & EPA 94), 10 samples for ICP-MS (200.8 - EPA 91 & EPA 94)). If the method does not specify a frequency or criteria, a minimum frequency of 1/20 and at the end of the run is required.

Successful analysis of the check standard indicates that instrument drift and response are stable enough for analysis to continue, i.e., the calibration performed this morning is still valid for this afternoon's samples.

9. A Laboratory Fortified Blank (spiked blank) is prepared with each digestion batch (group of samples processed together) at a concentration at or near the regulatory limit, or as specified in the methods and analyzed within criteria (required 200.7, 200.9). (200.7, 200.8, 200.9 - EPA 91 & EPA 94)

The Laboratory Fortified Blank assesses recovery of the analyte(s) of interest through the entire analytical procedure (preparation and analysis) in lab pure water, and is a measure of Accuracy (Bias) of the results.

10. Laboratory Fortified Samples (Method Spike Duplicates). Spikes are prepared in duplicate at a 1/20 minimum frequency per facility per matrix. Spikes are to be made to result in concentrations at or near the regulatory limit, or as specified in the methods. The outfalls that are spiked are varied (rotated) so that all are eventually spiked. (Though several methods (3020 - SM 18; 200.7, 200.8, & 200.9 - EPA 91 & EPA 94); require laboratory fortified samples, and some (3020 - SM 18) require duplicates; not all require both. The State and EPA analytical and quality control experts agreed on Matrix Spike Duplicates as the most sensible approach to evaluate both the method precision and method accuracy relative to the sample matrix.)

The Laboratory Fortified Samples assess recovery of the analyte(s) of interest through the entire analytical procedure (preparation and analysis) in that particular sample matrix, and allow for the calculation of method precision. This QC measure helps assure that the entire analytical method (preparation and analysis) results in acceptable recovery of the analytes of interest in the sample matrix being investigated.

For Graphite Furnace AAS, all unknowns quantified by methods other than 200.9 must be checked for significant matrix interferences by serial dilution (10% Relative Percent Difference (RPD) as $(X_1 - X_2) / \text{AVG}.X * 100$) or single post digestion spike (85-115% Recovery). If matrix effects are significant the

unknowns are quantified by the method of standard additions (MSA). (All Furnace Methods - EPA 79/83; 3113 - SM 18)

Graphite Furnace AAS, while much improved in recent years, remains exceptionally prone to matrix effects caused by sample constituents other than the analyte of interest. These unpredictable effects can produce either positive or negative bias.

11. Method Detection Limit (MDL) studies are performed initially and repeated at least yearly or with a significant change in the procedures (new method, new analytical instrument, different analyst, major equipment repair, etc.). The data obtained verifies ability to meet program requirements, and must be documented and appropriate for the permit limit. The MDL procedure is described in 40 CFR Part 136, Appendix B. (3020 - SM 18; 200.7, 200.8, 200.9 - EPA 91 & EPA 94)

MDL studies provide the data to document that data reported above the quantification limit (i.e., the lowest standard, currently referred to as the Minimum Level or "ML") is above the MDL, and is not due to noise. EPA recommends that the lowest calibration standard (ML) be at least 3.18 x MDL (based on the EPA DRAFT Below Detection Guidance and discussion in the Supplementary Information Document for the Great Lakes Guidance), although States and Tribes have the discretion to develop other credible procedures for deriving an ML. Methods 200.7, 200.8, and 200.9 also use the MDL to assess the Laboratory Reagent Blank (Method Blank).

12. Documentation: The analytical methods used, digestion logs, and all raw data (instrument data) and processed sample and QC data are retained on file for at least 3 years (Permit requirement). The documentation must be sufficient to reconstruct all calculations. If a commercial lab is employed the following information must be included in the data reports to the facility: holding time, preservation check results, method, units, analyst and any "not acceptable" QA/QC results. The facility must assure that the commercial laboratory retains the supporting raw data for the analytical results as is required of a facility laboratory. 1

Remedial actions are properly performed and documented following QC failures. Reanalysis is to be performed if the samples are still within holding times and properly preserved. If the problem can not be resolved or the samples can not be reanalyzed, then the results are to be reported and the results flagged (as described above).

13. Additional QC Items:

- a. Documentation of Standards:

The source and expiration dates of stock solutions recorded.

The date of standard preparation is recorded.
Standards are dated when received and when opened.

- b. Quality control data maintained for easy reference?
- c. Method manual available to analysts?
- d. QA Plan available to analysts?
- e. Instrument manual available to analysts?

GLOSSARY OF TERMS

Background Correction: Correction of analytical signal at the time of measurement to compensate for contribution from spectral effects caused by constituents in the sample other than the target analyte.

Check Standard: A calibration standard analyzed periodically throughout an analytical run to verify continued acceptable instrument performance.

Dissolved Metals (Dissolved): The concentration of analyte that will pass through a 0.45 micron filter assembly, prior to acidification. (EPA 91 and 40 CFR Part 136)

Duplicate Analyses or Measurements: The analyses or measurements of the variable of interest performed identically on two subsamples of the same sample. The results from duplicate analyses are used to elevate analytical or measurement precision but not the precision of sampling, preservation, or storage internal to the laboratory. (QAMS)

Equipment Blank (Sampling Equipment Blank): A clean sample (e.g., distilled water) that is collected in a sample container with the sample collection device and returned to the laboratory as a sample. Sampling equipment blanks are used to check the cleanliness of sampling devices. (QAMS)

Field Blank: A clean sample (e.g., distilled water), carried to the sampling site, exposed to sampling conditions (e.g., bottle caps removed, preservatives added) and returned to the laboratory and treated as an environmental sample. Field blanks are used to check for analytical artifacts and/or background introduced by sampling and analytical procedures. (QAMS)

Flame Atomic Absorption: Method for determination of metals involving the aspiration of standards and samples into a flame to produce a cloud of ground state atoms which are measured spectrometrically through the absorption of light emitted by a wavelength-specific hollow cathode or electrodeless discharge lamp.

Graphite Furnace Atomic Absorption: Method for determination of metals involving the heating of standards and samples on a graphite surface to produce a cloud of ground state atoms which are measured spectrometrically through the absorption of light emitted by a wavelength-specific hollow cathode or electrodeless discharge lamp.

Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES): Method for the determination of metals involving the aspiration of standards and samples through a high-temperature plasma to produce excited atoms and ions which are measured spectrometrically through the emission of light.

Interelement Correction: Mathematical correction of analytical signal after measurement to compensate for direct overlap of structural spectra caused by constituents in the sample other than the target analyte(s).

Lab Fortified Blank (Spiked Reagent Blank): A specified amount of reagent blank fortified with a known mass of the target analyte; usually used to determine the recovery efficiency of the method. (QAMS)

Laboratory Fortified Samples (Spiked Sample): A sample prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Spiked samples are used, for example, to determine the effect of the matrix on a method's recovery efficiency. (QAMS)

Lab Pure Water (Pure Reagent Water): Water in which an interferant is not observed at the MDL of the parameters of interest. (40 CFR Part 136)

Linear Working Range (Linear Dynamic range): The concentration range over which the analytical curve remains linear. (EPA 91)

Matrix Effect: The enhancement or suppression of analytical signal caused by constituents in the sample other than the target analyte. (EPA 91)

Matrix Modifier: A substance added to the graphite furnace along with the sample in order to minimize the interference effects by selective volatilization of either analyte or matrix components. (EPA 91)

Method Blank: A clean sample processed simultaneously with and under the same conditions as samples containing an analyte of interest through all the steps of the analytical procedure. (QAMS)

Method Detection Limit (MDL): The minimum concentration of an analyte that, in a given matrix and with a specific method, has a 99% probability of being identified, qualitatively or quantitatively measured, and reported to be greater than zero. (QAMS)

Method of Standard Additions (Standard Addition): The procedure of adding known increments of the analyte of interest to a sample to cause increases in detection response. The level of analyte of interest present in the original sample is subsequently established by extrapolation of the plotted responses. (QAMS)

Precision: The degree to which a set of observations or measurements of the same property, usually obtained under similar conditions, conform to them; a data quality indicator. Precision is

usually expressed as standard deviation, variance or range, in either absolute or relative terms. (QAMS)

Quality Assurance (QA): An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence. (QAMS)

Quality Assurance Plan: A written description of the laboratory's quality assurance activities. (NELAC)

Quality Control (QC): The overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users. The aim is to provide quality that is satisfactory, adequate, dependable, and economical. (QAMS)

Reagent Blank: A sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps to error in the observed value. (QAMS)

Reference Material: A material or substance, one or more properties of which are sufficiently well established to be used for the calibration of an apparatus, the assessment of a measurement method, or assigning values to materials. (QAMS)

Standard Curve (Calibration Curve): The graphical relationship between the known values for a series of calibration standards and instrument responses. (QAMS)

Total Metals: The concentration of metals determined on an unfiltered sample following vigorous digestion (Section 4.1.3), or the sum of the concentrations of metals in the dissolved and suspended fractions. (EPA 79/83 and 40 CFR Part 136)

Total Recoverable: The concentration of an analyte determined in an unfiltered sample following treatment by refluxing with hot, dilute mineral acid. (EPA 91 and 40 CFR Part 136)

QAMS: "Glossary of Quality Assurance Terms", U.S. EPA, Quality Assurance Management Staff, August 31, 1992.

NELAC: National Environmental Laboratory Accreditation Conference, Draft Standards, State/EPA Focus Group, June 1994.

EPA 91: EPA Methods for the Determination of Metals in Environmental Samples, June 1991.

EPA 79/83: EPA Methods for Chemical Analysis of Water and Wastes, 1979/83.

CFR 136: 40 CFR Part 136, Appendix C

SM 18: Standard Methods for the Examination of Water and Wastewater, 18th edition, 1992

EPA 94: Methods for the Determination of Metals in Environmental Samples, EPA/600/R-94/111, May 1994

**MERCURY BY MANUAL COLD VAPOR
EPA Method 245.1
General Checklist**

40 CFR Part 136 Reference: 1979/83 US EPA Manual "Methods for Chemical Analysis of Waters and Wastes

Sample Collection, Preservation, and Holding Times:

Samples for total mercury are unfiltered samples preserved with nitric acid in the field to a pH of <2 (245.1-1).

All glassware and plasticware used washed with detergent and tap water, rinsed with 1+1 nitric acid, tap water, 1+1 hydrochloric acid, tap water, and final DI water rinse? (METALS-4,5) If not, blanks must be used to document that the procedure and materials in use are acceptable. (METALS-5, NOTE-2)

Are the sample collection containers trace element free (acid cleaned or single use from a reliable source)? If the cleaning procedure in the methods manual is not used, blanks must be used to document that the procedure and materials in use are acceptable. (METALS-5, NOTE-2)

Samples for dissolved metals are filtered through a 0.45 micron filter as soon as possible and preserved after filtration with nitric acid to a pH of <2. (METALS-5)

For dissolved metals is the filtration apparatus and filter rinsed with 50-100 ml of sample and the filtrate discarded prior to filtering the aliquot to be preserved as the dissolved metals sample? (METALS-5)

Apparatus:

Atomic Absorption Spectrometer with mercury lamp, set up to manufacturer's recommended conditions for mercury, or a commercial mercury system. (245.1-2)

A variable speed recorder compatible with the system used, or electronic data collection. (245.1-2)

Absorption cells must have quartz windows and be at least 10 cm long. Cell must be able to be placed in the light path and adjusted for maximum transmittance. (245.1-2)

The air pump (peristaltic pump) must be capable of delivering 1 l/min. (245.1-2)

The flowmeter must be capable of measuring 1 l/min. (245.1-2)

The aeration tubing used in the BOD bottles is a straight glass frit of coarse porosity. (245.1-2)

The drying tube is a 6" long, 3/4" diameter tube containing 20 g of magnesium perchlorate. Its purpose is to prevent water vapor from entering the absorption cell. A small reading lamp directed on the absorption cell to warm it may be substituted for the drying tube. (245.1-2)

Reagents (245.1-3):

Sulfuric acid: Concentrated reagent grade
0.5 N (14.0 ml to 1l)

Nitric Acid: Concentrated reagent grade of low mercury content
NOTE: If blanks are high, trace metals grade or redistilled acid may be necessary.

Stannous Sulfate: 25g to 250 ml 0.5 N sulfuric acid (stannous chloride may be substituted)
NOTE: This mixture is a suspension and must be stored continuously during use.

Sodium Chloride-Hydroxylamine Sulfate Solution: 12g sodium chloride and 12g hydroxylamine sulfate in DI water to 100 ml final volume.

Potassium Permanganate: 5% solution, w/v (5g to 100 ml final volume)

Potassium Persulfate: 5% solution, w/v (5g to 100 ml final volume)

Standards:

Primary Stock Solution may be prepared from mercuric chloride (245.1-3) or purchased.

Is purchase date of the solution within the expiration date?

Is the working mercury solution prepared fresh each day of use at a concentration of 0.1 $\mu\text{g/ml}$ in 0.15% nitric acid? (245.1-4)

Are the calibration standards prepared by transferring 0.05, 1.0, 2.0, 5.0, and 10.0 ml aliquots of working solution to 300 ml BOD bottles with DI water added to a final volume of 100 ml? (245.1-4)

Standards digested and processed the same as samples? (245.1-4)

Procedure:

Are aliquots of 100 ml of sample or an aliquot diluted to 100 ml transferred to a BOD bottle? (245.1-4)
4) An aliquot of 200 ml may be used if increased sensitivity is required. (245.1-6)

Does the aliquot contain not more than 1.0 μg Hg? (245.1-4)

Was the sample well-mixed before the aliquot was taken?

Are the following digestion reagents added to standards and samples? (245.1-4):

5 ml conc sulfuric acid, mix

2.5 ml conc nitric acid, mix

15 ml potassium permanganate, mix, wait 15 minutes.

If purple color does not persist, add additional permanganate, mix, wait 15 minutes; continue until the purple color persists for at least 5 minutes after the addition of the permanganate.

8 ml potassium persulfate

Are the samples heated in a hot water bath maintained at 95 degrees C for 2 hours? (p. 245-4)

Does the hot water bath have a cover to maintain a steady temperature?

Does the 2-hour timing begin upon placing bottles in the bath or when the bath has reached 95 degrees?

Is the thermometer used in the bath checked periodically against a NIST thermometer (or traceable to NIST)?

After 2 hours are the bottles removed and allowed to cool before the addition of hydroxylamine. (245.1-4)

Is 6 ml of hydroxylamine solution added per bottle to reduce excess permanganate? (245.1-4)

After a delay of at least 30 seconds, is 5 ml of stannous sulfate solution added? (245.1-4 & 5)

Is the bottle immediately attached to the aeration apparatus? (245.1-4 & 5)

Is the circulation pump allowed to run continuously at a rate of 1 l/min? (245.1-4)

Is the absorbance allowed to reach a maximum? (245.1-4)

Is the system purged and the recorder allowed to return to minimum value before proceeding with the next bottle? (245.1-4)

Are the mercury vapors from the cell either vented or passed through a trapping solution or through activated charcoal? (245.1-4)

Calculation:

Is a standard curve constructed by plotting peak height versus micrograms of mercury? (245.1-4)

Are the peak heights of the unknowns and the standard curve used to determine the micrograms of mercury per bottle? (245.1-5)

Is the concentration of mercury calculated by the formula on p. 245.1-5?

$$\mu\text{g Hg/L} = (\mu\text{g Hg in aliquot}) \times \frac{1000}{\text{volume of aliquot in ml}}$$

Are the mercury concentrations reported as follows? (245.1-5)

below 0.2 $\mu\text{g/L}$, <0.2 $\mu\text{g/L}$

1-10 $\mu\text{g/L}$, one decimal

above 10 $\mu\text{g/L}$, whole numbers

Do the standards cover the concentration range desired (samples above high standard are diluted and repressed)? (METALS-10)

NOTE: Commercial systems exist that have automated the reduction step in this method. If only a portion of digested is used for reduction, the volume of permanganate in excess of 15 ml must be recorded and applied in the calculation as a dilution factor.

Data Keeping:

(Required by Permit _____)

Are the permit levels met by the analytical technique chosen?

All data legible and traceable?

Analysts initials, analysis time and date recorded?

Are all raw data retained for at least 3 years?

Equipment Used:

Suggestions:

Periodic and closing check standards

Spiked samples (1/10 suggested frequency)

Duplicate sample analyses (1/10 suggested frequency)

Periodic analysis of Audit solutions to confirm performance of instrument and accuracy of standards.

Check high unknowns for possible absorbing organics by performing analysis without the reductant (stannous sulfate).

Log of beginning and ending hot water bath times and temperatures.

If persistent contamination of glassware is a problem, the BOD bottles can be baked out at high temperatures in a programmable oven.

References:

NOTE: As of this writing (4/95), SM 18 and EPA 79/83 are CFR listed method references. Method 200.8 (version not specified, but EPA 91 implied by document date) has been allowed for use in NPDES analyses by a letter from EMSL-CI to the Regional Administrator in 1992. EPA 94 is the listed method reference for methods 200.7, 200.8, and 200.9 in the most recent Proposed Rules for 40 CFR Part 136.

1. **Guidance on the Documentation and Evaluation of Trace Metals Data Collected for Clean Water Act Compliance Monitoring - EPA 821-B-95-002 - April 1995**
2. **Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels - EPA 821-R-95-034 - April 1995**
3. **Monitoring Trace Metals at Ambient Water Quality Criteria Levels: Issues, Plans, and Schedule, April 1994, USEPA, Office of Water, Office of Science and Technology Engineering and Analysis Division (4303).**
4. **Method for Sampling Ambient Water For Determination of Metals at EPA Ambient Water Quality Criteria Levels.**
5. **Quality Control Supplement for Determination of Metals at Ambient Water Quality Criteria Levels Using EPA Metals Methods, June 1994, USEPA, Office of Science and Technology Engineering and Analysis Division (4303).**
6. **"NPDES Self-Monitoring Data and Data Audit Inspection (DAIs)", Fall 1992, USEPA, CRL Region III.**
7. **QAMS - "Glossary of Quality Assurance Terms", USEPA, Quality Assurance Management Staff, August 31, 1992.**
8. **National Environmental Laboratory Accreditation Conference, Draft Standards, State/EPA Focus Group, June 1994.**
9. **"EPA Methods for the Determination of Metals in Environmental Samples", June 1991.**
10. **"EPA Methods for Chemical Analysis of Water and Wastes", 1979/83.**

- 11. "U.S. Geological Survey Protocol for the Collection and Processing of Surface-Water Samples for the Subsequent Determination of Inorganic Constituents in Filtered Water", Open-File Report 94-539, USGS.**
- 12. CFR 136: 40 CFR Part 136, Appendix C**
- 13. SM 18: Standard Methods for the Examination of Water and Wastewater, 18th edition, 1992**
- 14. EPA 79/83: Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, 1979/1983**
- 15. EPA 91: Methods for the Determination of Metals in Environmental Samples, EPA/600/4-91/010, June 1991**
- 16. EPA 94: Methods for the Determination of Metals in Environmental Samples, EPA/600/R-94/111, May 1994**
- 17. EPA Region III Metals' Data Position Paper - May 1, 1995.**